Supporting Information:

Reversibly Compressible and Freestanding Monolithic Carbon Spherogels

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Figures



Figure S1. (A) Size distribution of PS nanospheres obtained by dynamic light scattering (Z-average = 250.8 nm, PdI = 0.015); (B) Zeta potential measurement of PS nanosphere solution showing an average value of -18.5 mV within 12 runs.



Figure S2. SEM image of the used PS spheres (PS010). For sample preparation, a solution droplet was deposited on a carbon pad, dried and sputtered with a gold film to avoid charging effects.



Figure S3. TGA analysis (under Ar atmosphere) of the carbonization process of the sample CA_4 (green) and the reference sample without PS (red) and the PS starting colloidal solution (blue). Residual masses at 1000 °C are 47% (red), 36% (green), and 0% (blue).



Figure S4. High angle annular dark field (HAADF) scanning transmission electron microscopy image (STEM) of sample CA_7.2 with an energy dispersive X-ray spectroscopy (EDX) line scan across the hollow sphere for C and O.



Figure S5. (A) Transmission electron micrograph of a 50-nm sized PS templated carbon aerogel and (B) corresponding nitrogen sorption isotherms (solid dots: adsorption, empty dots: desorption).



Figure S6. Raman spectra of the PS templated and the reference sample (532 nm laser wavelength; power on the sample: 4 mW).



Figure S7. Chronological succession of reversible compressibility tests (up to 10% compression with a rate of 5 mm min⁻¹) during the mechanical testing experiments. Samples with an equal diameter were used.



Figure S8. (A) Nitrogen sorption isotherms measured at -196 °C and (B) cumulative pore size distributions (QSDFT, assuming slit pore geometry) for CO_2 activated carbon aerogels with different polystyrene concentrations and the pristine reference sample (without templating). (C) Differential pore size distribution pattern calculated from the data shown in panel (B).



Figure S9. (A-D) SEM images of the spherogel and reference samples after activation with CO_2 at 925 °C.

Electrochemical testing

Electrochemical characterization was carried out after crushing the material in a mortar and admixing 10 mass% of polytetrafluoroethylene to consolidate free-standing electrodes with a thickness of ca. 120 μ m and a diameter of 12 mm; the electrodes had a geometric density of 0.2-0.3 g cm⁻³. All measurements were done in a full-cell configuration with a carbon (YP80-F, Kuraray) spectator reference electrode. We used 1 M TEA-BF₄ (tetraethylammonium tetrafluoroborate) in acetonitrile (BASF, battery grade) as the electrolyte and a GF/D glass-fiber separator (Whatman). The cells were assembled in an argon-filled glove box (MBraun Labmaster; O₂, H₂O <1 ppm). Some reference measurements were carried out with the commercial activated carbon YP-80F (Kuraray) with a geometric density of 0.5 g cm⁻³. All the electrochemical measurements were conducted with a VMP300 potentiostat/galvanostat from BioLogic. Capacitance values were derived from the galvanostatic discharge profiles and normalized to the active mass of the electrodes. Our galvanostatic data were measured, including a short holding period at the vertex potential of 20 s, as can be seen from the galvanostatic charge/discharge profiles.

The cyclic voltammograms for all samples (**Fig. S10A**), including a reference sample composed of commercially available activated carbon, show a rectangular shape within the stable electrochemical cell voltage window up to 2.5 V for a scanning rate of 1 mV s⁻¹. The corresponding galvanostatic charge/discharge profiles are of the pronouncedly triangular shape (**Fig. S10B**) at a specific current of 0.25 A g⁻¹, indicative of capacitive systems based on the formation of an electrical double-layer. The samples CA_3, CA_6, and the pristine sample show at a low rate (0.1 A g⁻¹) a very similar specific capacitance of 105 F g⁻¹, 106 F g⁻¹, and 107 F g⁻¹, respectively, which is slightly higher than for commercially available activated carbon (type YP-80F) with 100 F g⁻¹. However, the rate handling ability is far superior as compared to activated carbon; as can be seen from **Fig. S10C**, all spherogel electrodes maintain about 92% of the initial low-rate capacitance at a high current of 10 A g⁻¹, whereas commercially available activated carbon loses about 40%. The enhanced rate handling ability aligns with the short diffusion path length across the nanoporous shell compared to long diffusion channels across micrometers-sized activated carbon particles.



Figure S10. Electrochemical characterization of a YP-80F carbon reference material, a non-templated pristine CA and carbon spherogels CA_3 and CA_6 in full-cell configuration with a spectator electrode (carbon) using 1 M TEA-BF₄ in acetonitrile. (A) Cyclic voltammetry recorded at 1 mV s⁻¹. (B) Galvanostatic charge/discharge profiles recorded at 0.25 A g⁻¹. (C) Electrochemical rate handling plots in the range of 0.1 A g⁻¹ to 100 A g⁻¹.

Tables

Sample	Band	Position (cm ⁻¹)	FWHM (cm ⁻¹)	I _D /I _G	
CA_2	D-mode	1346	11	0.86	
	G-mode	1584	66		
CA_4	D-mode	1345	11	0.86	
	G-mode	1583	65		
CA_7.2	D-mode	1346	11	0.97	
	G-mode	1586	59	0.07	
Reference	D-mode	1345	11	0.97	
	G-mode	1584	59	- 0.87	

Table S1. Characteristic Raman data listing the position of D- and G band, the FWHM, and I_D/I_G ratio.

Table S2. Physical properties of CO_2 activated carbon aerogels (CA) templated with different polystyrene concentrations (CA_1.5, CA_3, CA_6) including the reference sample (without polystyrene templating) obtained from N₂ sorption evaluation (QSDFT) and TEM micrographs.

Sample	SSA (QSDFT) (m ² /g)	Inner diameter (TEM) (nm)	Wall thickness (TEM) (nm)	Pore volume* (QSDFT) (cm ³ /g)	Micropore volume ** (QSDFT) (cm ³ /g)		
Reference	1859	-	-	1.10	0.74		
CA_1.5	1681	215	76	0.68	0.62		
CA_3	1773	216	47	0.74	0.58		
CA_6	1861	220	25	0.98	0.69		
* < 20 mm ** < 2 mm							

* < 30 nm;** <2 nm

SAXS Model

The model for fitting the SAXS curves is based on the autocorrelation function $\gamma_s(r)$ (see: Journal of Applied Physics 20(6) (1949) 518-525) of a hollow sphere with a homogeneous shell:

$$\gamma_{s}(r) = \begin{cases} \rho^{2} \left(\frac{4}{3} \left((R+t)^{3} - R^{3}\right)\pi - r((R+t)^{2}\pi + R^{2}) + \frac{r^{3}}{6}\pi\right) & r \leq t \\ \rho^{2} \frac{\pi}{2r}((R+t)^{4} + R^{4} - 2(R+t)^{2}R^{2}) & t < r \leq 2R \\ -\frac{\pi(r^{4} - 12r^{2}R^{2} + 16rR^{3} - 6t^{2}(2R+t)^{2})\rho^{2}}{12r} & 2R < r \leq 2R + t \\ \rho^{2} \left(\frac{4}{3} (R+t)^{3}\pi - r(R+t)^{2}\pi + \frac{r^{3}}{12}\pi\right) & 2R + t < r \leq 2(R+t) \\ 0 & 2(R+t) < r \end{cases}$$

where *R* is the radius of the core, *t* is the thickness of the shell and ρ is the electron density of the shell. This function is proportional to the probability that two random points in space at a given distance *r* are both within the shell.

The micropores are included in this model by a real space probability approach:

$$\gamma_m(r) = \begin{cases} \varphi + \frac{\sqrt{3}r - 6\sigma}{12\sigma^3} r^2 \varphi & r \le \sqrt{3}\sigma \\ \left(2 - r \frac{\sqrt{3}r^2 - 18r\sigma + 36\sqrt{3}\sigma^2}{36\sigma^3}\right) \varphi & \sqrt{3}\sigma < r \le 2\sqrt{3}\sigma \\ 1 - \varphi & 2\sqrt{3}\sigma < r \end{cases}$$

where $\gamma_m(r)$ is the probability that two random points within the microporous material are within the same phase. This function corresponds to a high probability to be within the same phase for small separations and a decay to a constant level determined by the volume fractions of micropores and material at large distances. The decay is described by a cubic B-spline, where σ is the square root of the decays variance. The cubic B-spline instead of a normal distribution has been chosen in order to allow for analytical expressions after Fourier transformation (see below).

Since both functions correspond to probabilities, the probability of two random points that are separated by a distance r to be within the shell of the sphere and not in a micropore is the product of these two functions:

$$\gamma(r) = \gamma_s(r)\gamma_m(r)$$

The scattering curve I(q) can be obtained by Fourier transformation:

 $I(q) = 4\pi \int_0^\infty \gamma(r) r^2 \frac{\sin qr}{qr} dr$ The polydispersity of the radius of the core σ_R , and of the thickness of the shell σ_t were included by convolution of the scattering curve:

$$I'(q) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} s(x)s(y)I(q, R + x\sigma_R, t + y\sigma_t) dxdy$$

where s(x) denotes a cubic B-spline:

$$s(x) = \begin{cases} 0 & x \le -2\sqrt{3} \\ \frac{4}{\sqrt{3}} + \frac{1}{18}x(36 + 6\sqrt{3}x + x^2) & -2\sqrt{3} < x \le \sqrt{3} \\ \frac{2}{\sqrt{3}} - \frac{1}{6}x^2(2\sqrt{3} + x) & \sqrt{3} < x \le 0 \\ \frac{1}{6}(4\sqrt{3} - 2\sqrt{3}x^2 + x^3) & 0 < x \le \sqrt{3} \\ \frac{4}{\sqrt{3}} - \frac{1}{18}x(36 - 6\sqrt{3}x + x^2) & \sqrt{3} < x \le 2\sqrt{3} \\ 0 & 2\sqrt{3} < x \end{cases}$$

The resulting scattering curve is completely analytical due to the simple integration of the B-splines.