

## ***Supporting Information***

### **Hybrid Carbon Spherogels: Carbon Encapsulation of Nano-Titania**

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## Experimental Section

### Materials and Synthesis

An aqueous monodisperse polystyrene (PS) colloidal solution with a concentration of 3 mass% was used as a templating agent. The PS spheres (270 nm, 0.025 Pdl, **Fig. S1** and SEM image in **Fig. S1**), were prepared via emulsion polymerization of styrene with potassium persulfate (KPS) as initiator and polyvinylpyrrolidone (PVP) as a stabilizing agent, as described previously.[1]

Resorcinol, formaldehyde (37 mass%), ethanol (96 %), and sodium carbonate were used without further purification.  $\text{Ti}(\text{acac})_2(\text{OiPr})_2$  (75 mass%) in isopropanol was used as Ti source. A pristine, titania-free sample was prepared without the Ti-precursor. After mixing the educts and PS colloidal solution in a beaker and adding sodium carbonate as a catalyst, the pH was adjusted to 5.42. The sol was further stirred for 1 h at a low speed. Afterward, the sol was poured into glass molds with 12.5 mm diameter size and placed in an 80 °C tempered oven for 7 days. Solvent exchange to acetone followed with a daily change to fresh acetone within 3 days. The samples were supercritically dried with  $\text{CO}_2$  at 110 bar and 60 °C and afterward carbonized in a tube furnace under constant Ar flow at 800°C with a dwell time of 2 h (CS- $\text{TiO}_2/\text{C}$  800). Two subsequent sample treatments were performed: (1) Thermal annealing under Ar up to 1100 °C to yield CS- $\text{TiO}_2/\text{C}$  1100; (2) Increasing the titania content by controlled gaseous etching of carbon in a  $\text{CO}_2$  stream with 30 min dwell time at 800 °C (CS- $\text{TiO}_2/\text{C}$  30 min).

## Material Characterization

The morphologies of carbon spherogels were analyzed with a Zeiss Ultra Plus field emission scanning electron microscope (SEM) using an in-lens secondary electron detector. The acceleration voltage was adjusted between 2 kV to 5 kV. Transmission electron microscope (TEM) images were recorded with a JEOL JEM F200 TEM, equipped with a cold field emission source, using a TVIPS F216 2k by 2k CMOS camera. An accelerating voltage of 200 kV was used. Thermogravimetric analysis (TGA) was carried out with a NETZSCH STA 449 F3 Jupiter device from 20 °C to 1000 °C with a heating rate of 10 °C/min using argon or synthetic air atmosphere.

Sorption isotherms were obtained with an Autosorb-iQ (Anton Paar) apparatus. Samples were degassed under vacuum for 24 h at 250 °C. Measurements were done at -196 °C using nitrogen and at 0 °C using carbon dioxide. Pore size distributions were calculated using a slit pore model and quenched-solid density functional theory (QSDFT) for nitrogen sorption. Only the adsorption branch was used due to the cavitation effect during desorption. Pore size distributions from carbon dioxide isotherms were calculated using the NLDFT slit pore model. Dynamic light scattering (DLS) and zeta potential measurements were performed with a Malvern Zetasizer instrument. A light-backscattering angle of 173° was adjusted to record the data. Each measurement contains 30 separate DLS measurements with 3 sub-runs each of 10 s duration.

The in situ XRD measurements were conducted using a gas-tight heating chamber installed inside an XPERT III: PANalytical XPert Pro MPD diffractometer under constant Ar flow of 200 mL/min. In a single measurement, the as-prepared composite material was placed in the chamber, and a room temperature XRD scan (25 °C) was taken to ensure correct sample positioning. The sample was then heated up to 800 °C with a quick ramp of 10 °/min to reach the annealing state used to prepare the composite. After reaching this temperature, X-ray diffraction patterns have been recorded with the temperature interval of 50 °C, while applying the same heating ramp; however, the heating was stopped every time the aimed temperature was reached (850, 900, 950, 1000, 1050, 1100 °C) and XRD data collection was in progress. XRD was recorded in the  $2\theta$  interval of 22 to 48° to speed up the data collection while scanning the most relevant diffraction angles.

Raman spectra were recorded with 532 nm laser excitation and 4 mW power on the sample by a Raman microscope DXR2 from Thermo Fisher Scientific, equipped with a 10x objective (laser spot 2.1  $\mu\text{m}$ ).

Small angle x-ray scattering (SAXS) experiments of samples CS-TiO<sub>2</sub>/C 800 and CS-TiO<sub>2</sub>/C 1100 were measured using a Nanostar (Bruker AXS) equipped with a 1 $\mu\text{S}$  microsource (Incoatec) using Cu-K $\alpha$  radiation and 300  $\mu\text{m}$  SCATEX pinholes (Incoatec). The scattering patterns were recorded using a VÅNTEC-2000 detector (Bruker AXS). SAXS measurements of sample CS-TiO<sub>2</sub>/30 min were performed using a Nanostar equipped with a sealed tube X-ray source using Cu-K $\alpha$  radiation and 500  $\mu\text{m}$  SCATEX pinholes. The scattering patterns were recorded using a VÅNTEC-500 detector (Bruker AXS). In all cases, samples were positioned at sample-detector distances of 1052 mm and 675 mm to cover a wider angular range. Scattering angles were calibrated using a silver-behenate standard. Background scattering was subtracted after transmission correction. One dimensional scattering curves were obtained by integration resulting in intensities  $I(q)$  data, where the absolute value of the scattering vector is  $q=4\pi/\lambda \cdot \sin(\vartheta/2)$  using the wavelength  $\lambda$  and the scattering angle  $\vartheta$ . The scattering curves from the two detector positions were merged. The autocorrelation function was computed from the scattering curves using the indirect Fourier transformation.[2]

X-ray photoelectron spectroscopy (XPS) measurements were conducted on a custom lab-based system from SPECS GmbH, with details on the setup described in Ref [3]. The XPS spectra were recorded with monochromatic Al-K $\alpha$  radiation and the binding energy was calibrated to the C1s signal. Peak fitting was performed with the Casa XPS software, including background subtraction. To fit line shapes, Gauss-Lorentz sum functions were used for the titania and oxygen components, and the main carbon signal was fitted with an asymmetric line shape. For the Ti 2p signal a spin orbit splitting of 5.7 eV was used (NIST XPS database: [https://srdata.nist.gov/xps/main\\_search\\_menu.aspx](https://srdata.nist.gov/xps/main_search_menu.aspx)).

XPS spectra were recorded of the pristine carbon spherogel and the titania-loaded sample, both carbonized at 800 °C (pristine carbon spherogel and CS-TiO<sub>2</sub>/C 800). For the unloaded spherogels no titania signal was observed. After loading with titania, two species could be observed. The Ti 2p signal at ~458.9 eV can be attributed to TiO<sub>2</sub> [4] in the layer of the carbon spherogel, and the signal at ~455.1 eV could be either assigned to substoichiometric TiO<sub>x</sub>, to TiC or Ti-oxide in direct contact with the spherogel sample.[5]

In the C 1s signal, the titania loading also induced spectral changes. For unloaded spherogels three features could be observed. The signal at 284.2 eV from the spherogels with the corresponding plasmon at 289.6 eV and a small feature related to oxygen impurities at ~ 286.3 eV.[6] After loading with titania, a new signal appeared at 286.9 eV related to the Ti-oxide in direct contact with the spherogel. For the pristine spherogels a feature at ~532.7 eV could be observed in the O1s spectra, corresponding to minor amounts of oxygen impurities in the carbon spheres (no detailed peak fitting was applied due to the low signal intensity). After loading with titania, a new signal appeared at 534.1 eV that could be assigned to TiO<sub>2</sub>. Generally, both the Ti 2p and the O1s signal are weak, as the outer carbon spherogel shell is dampening the photoelectrons' pathway.

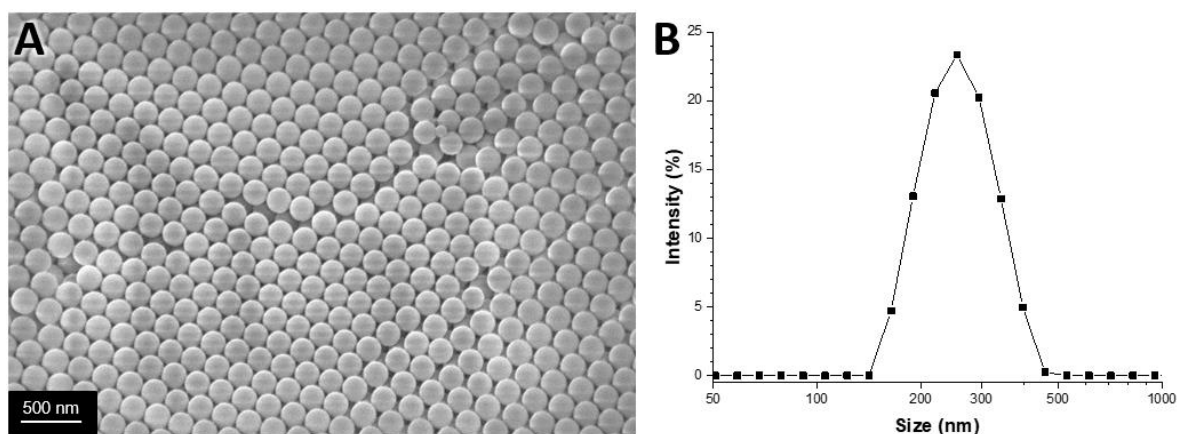
### Electrode preparation and electrochemical characterization

For the preparation of the working electrode, 90 mass% of synthesized CS-TiO<sub>2</sub>/C 800 or 90 mass% of CS-TiO<sub>2</sub>/C 30min were mixed with polyvinylidene fluoride (PVDF, Alfa Aesar) binder with a 10 mass% solution in N-methyl-2-pyrrolidone (NMP, Sigma Aldrich) without any further conductivity additive. The electrode slurries were doctor-bladed on a copper foil (25  $\mu$ m, MTI) using a 200  $\mu$ m doctor-blade and subsequently dried in a fume hood at ambient conditions. To remove remaining NMP, the electrodes were afterward dried in a vacuum at 110 °C overnight. The resulting electrode thickness was typically 125 $\pm$ 10  $\mu$ m with a material loading of 2.2 $\pm$ 0.5 mg/cm<sup>2</sup>.

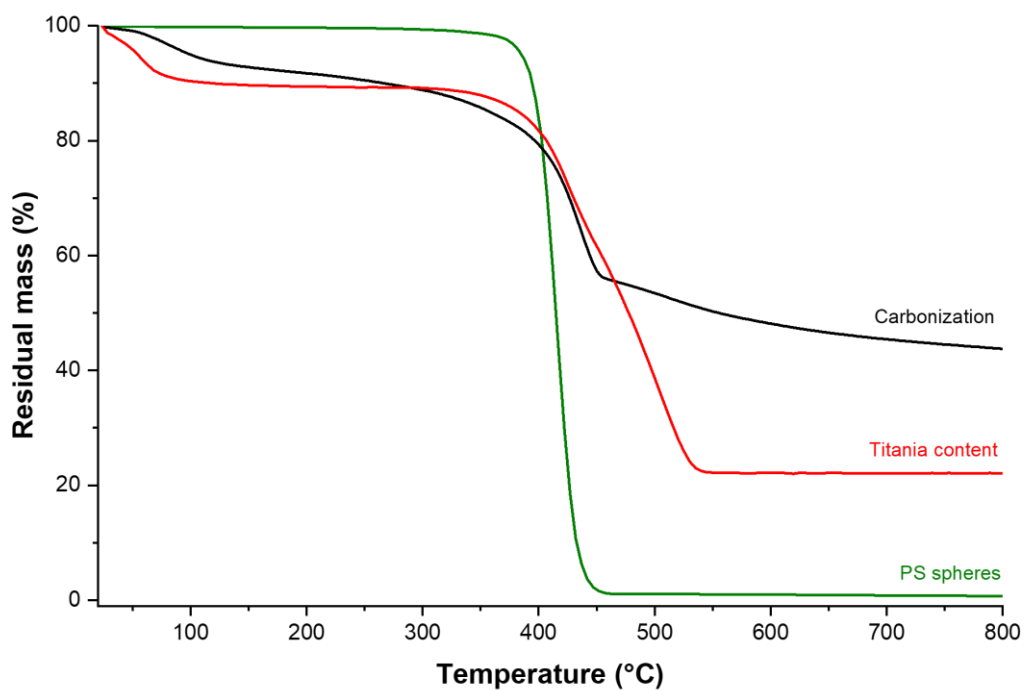
The coated electrodes were punched to 10 mm discs using press-punch (EL-CELL) and applied as the working electrode in CR2032 coin cells as a two-electrode set up for electrochemical benchmarking. All half-cells were prepared in an argon-filled glovebox (MBraun, O<sub>2</sub> and H<sub>2</sub>O < 0.1 ppm) with lithium discs (diameter of 11 mm) as a counter and a reference electrode, which are separated by two pieces of Celgard 2325 (diameter of 18 mm) from the working electrode. 1 M lithium hexafluorophosphate (LiPF<sub>6</sub>) salt dissolved in a mixture of ethylene carbonate and dimethyl carbonate (EC:DMC, 1:1 by volume, Sigma Aldrich) was used as the electrolyte.

Cyclic voltammetry (CV) electrochemical measurements were carried out using a VMP multichannel potentiostat/galvanostat from Bio-Logic science instruments equipped with the EC-Lab software, in a potential window from 1.0-3.0 V vs. Li<sup>+</sup>/Li with a scan rate of 0.1 mV/s. Further electrochemical measurements were carried out using a potentiostat/galvanostat from Arbin. To investigate the rate handling capability, galvanostatic charge/discharge cycling with potential limitation (GCPL) experiments were recorded at voltages in the range from 1.0-3.0 V vs. Li<sup>+</sup>/Li at different applied specific currents of 0.01-25 A/g. To quantify the cycling stability, a specific current of 0.1 A/g was used. In general, all electrochemical measurements were carried out in a climate chamber (Binder) with a constant temperature of +25 $\pm$ 1 °C.

## Supporting Figures

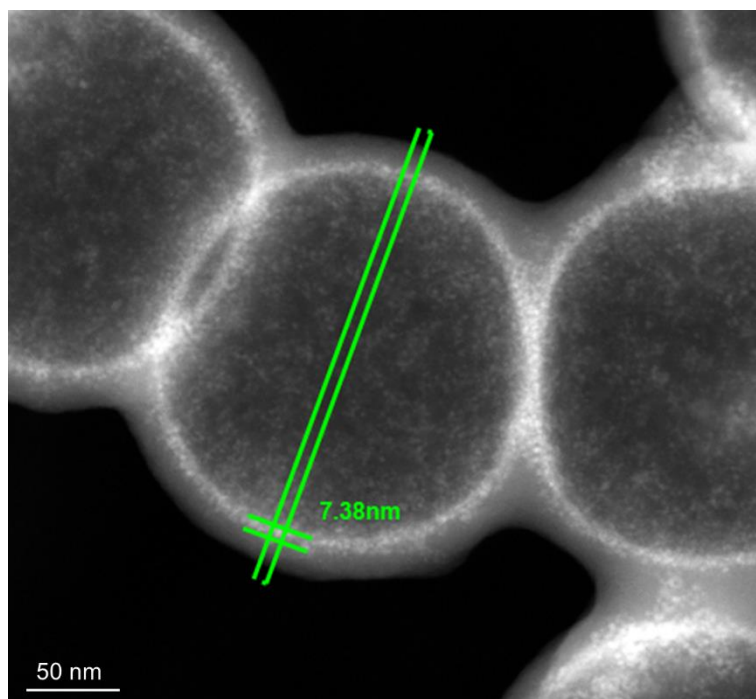


**Figure S1.** (A) Scanning electron micrograph of the used polystyrene spheres. For sample preparation, a solution droplet was deposited on a carbon pad, dried, and sputtered with a gold film to avoid charging effects. (B) Particle size distribution obtained by dynamic light scattering (Z-average = 250 nm, Pdl = 0.025).

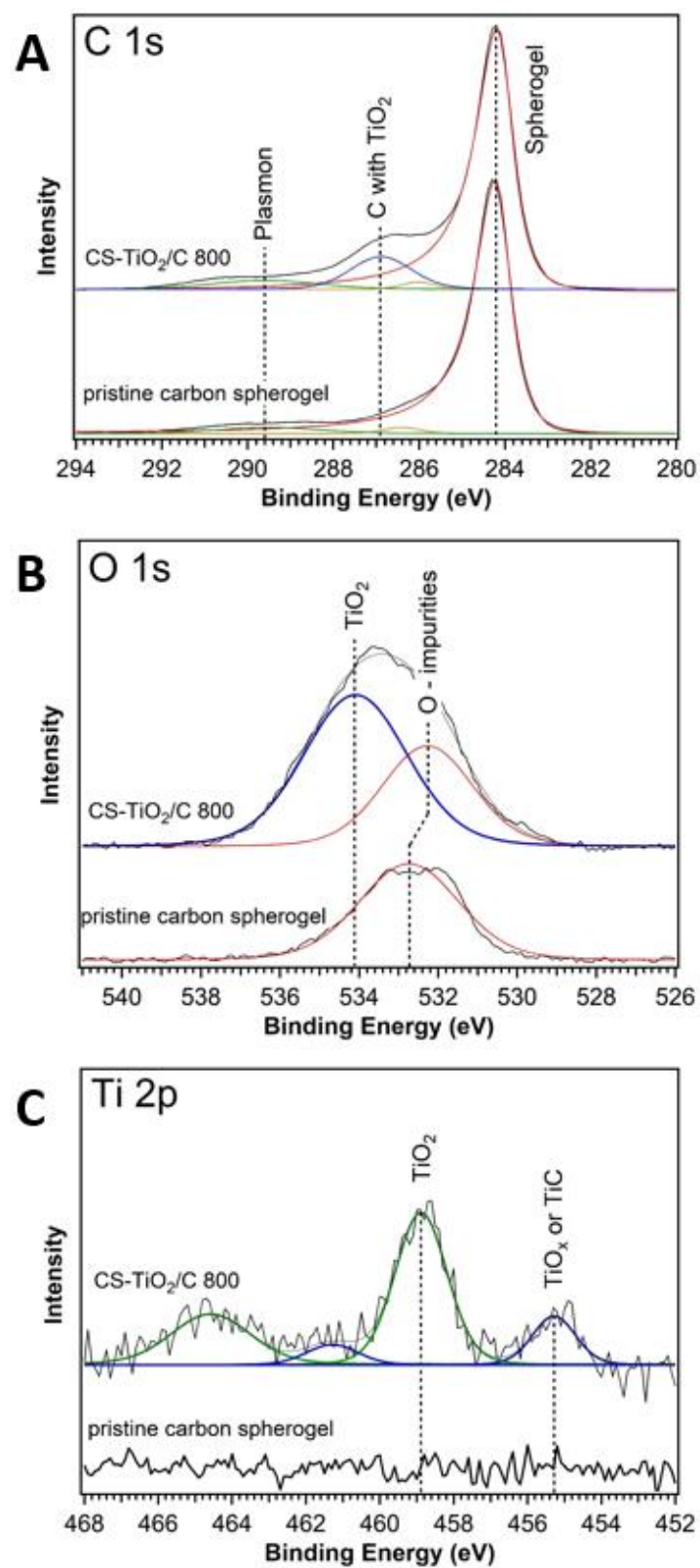


**Figure S2.** Thermogravimetric analysis (TGA) under Ar atmosphere of the carbonization process of the hybrid Ti-precursor-loaded, PS templated RF sample (black) and pure PS template sphere decomposition (green). The titania content of the final hybrid spherogel sample (red) is recorded under synthetic air (20% oxygen / 80% nitrogen) atmosphere.

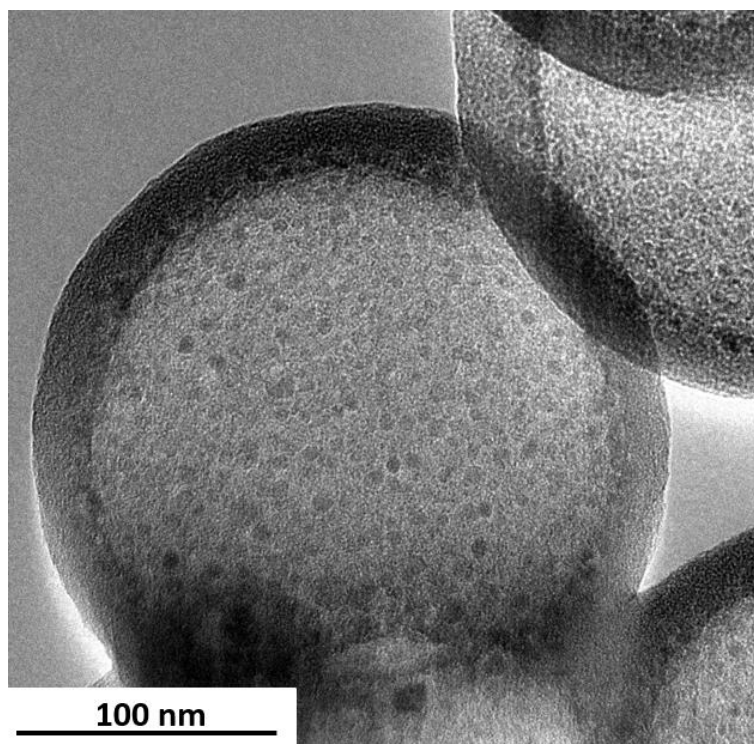




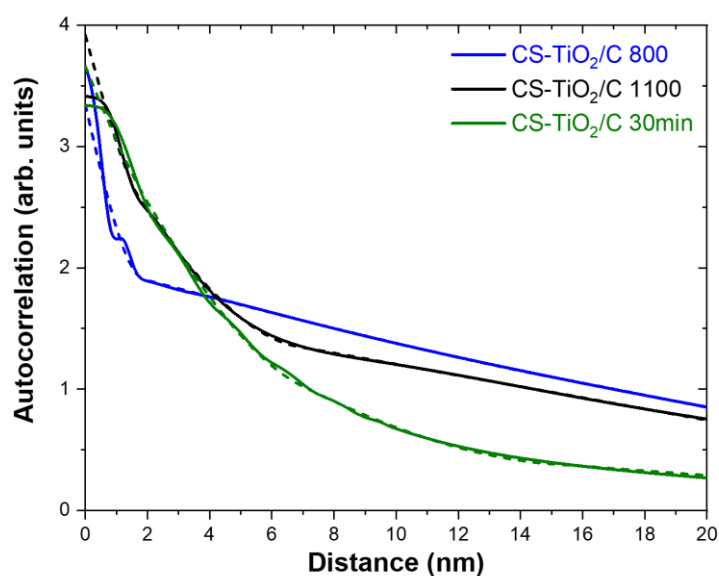
**Figure S3.** High angle annular dark-field (HAADF) scanning transmission electron micrograph of a titania/carbon hybrid spherogel sample CS-TiO<sub>2</sub>/C 800 with the green marked thickness of the titania layer.



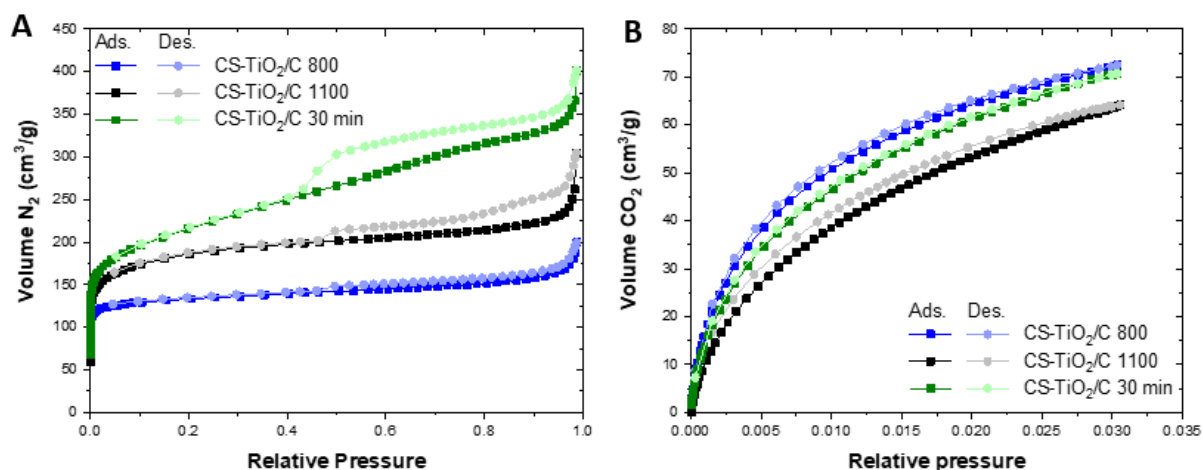
**Figure S4.** X-ray photoelectron spectra of (A) C 1s, (B) O 1s, and (C) Ti 2p of a pristine carbon spherogel sample and a titania-loaded one (CS-TiO<sub>2</sub>/C 800).



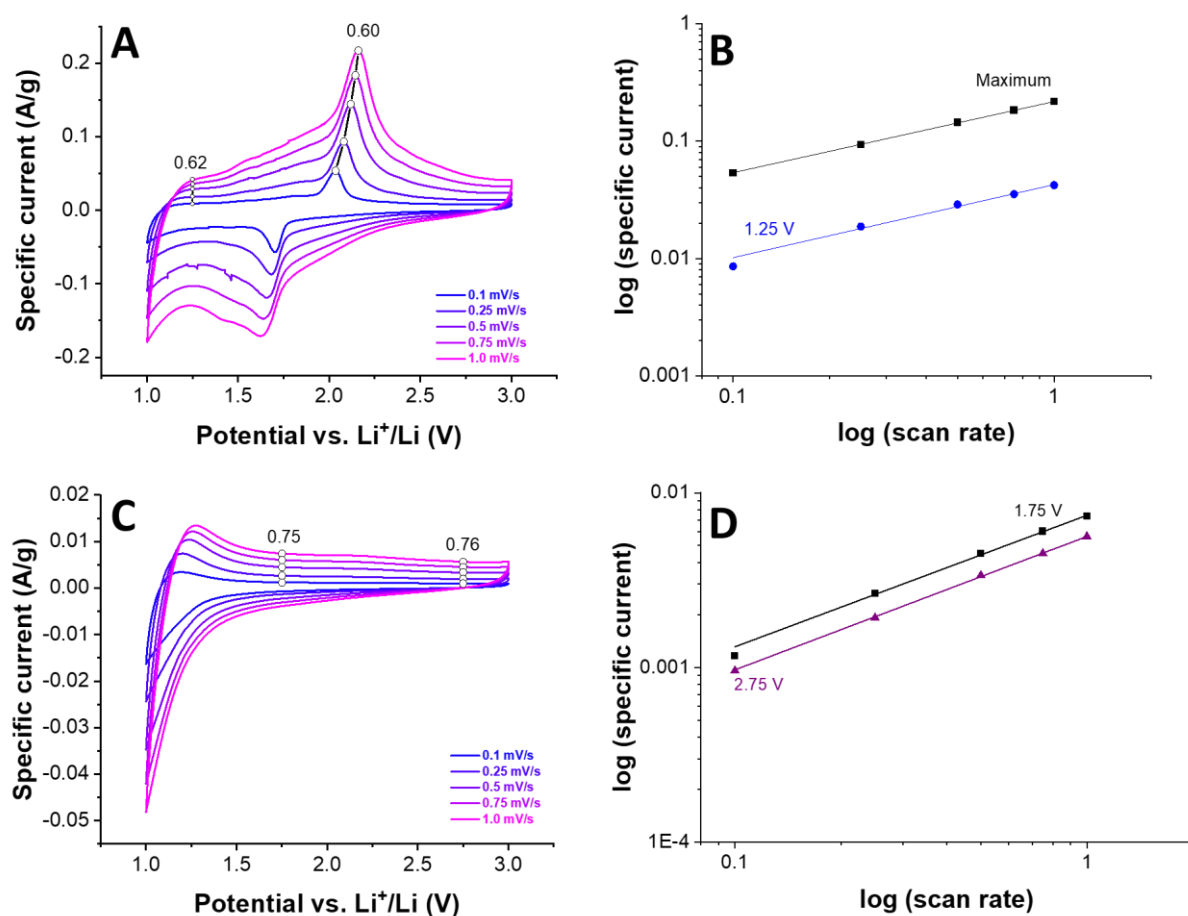
**Figure S5.** Transmission electron micrograph of the sample subjected to carbon dioxide annealing at 800°C for 30 min.



**Figure S6.** Autocorrelation function obtained from small-angle X-ray scattering data. The dashed lines correspond to model fits based on small globular structures (diameter 2 nm), a shell thickness of 35 nm, and for the annealed sample, additional globular structures (diameter 7 nm) and finally globular structures (diameter 15 nm) instead of the 2 nm structures after CO<sub>2</sub> treatment.



**Figure S7.** Nitrogen sorption isotherms measured at  $-196^{\circ}\text{C}$  (A) and carbon dioxide sorption isotherms measured at  $0^{\circ}\text{C}$  (B) for the as-prepared hybrid carbon spherogel CS-TiO<sub>2</sub>/C 800 (blue) and after heat treatment at  $1100^{\circ}\text{C}$  CS-TiO<sub>2</sub>/C 1100 (black/grey) as well as a 30 min  $\text{CO}_2$  activated sample CS-TiO<sub>2</sub>/C 30min (green).



**Figure S8.** Cyclic voltammograms at different scanning rates and kinetic fitting to calculate b-values. (A) CS-TiO<sub>2</sub>/C 30min, (B) CS-TiO<sub>2</sub>/C 800.

## Supporting References

- [1] X. Du, J. He, Facile size-controllable syntheses of highly monodisperse polystyrene nano-and microspheres by polyvinylpyrrolidone-mediated emulsifier-free emulsion polymerization, *Journal of Applied Polymer Science* 108(3) (2008) 1755-1760.
- [2] O. Glatter, A new method for the evaluation of small-angle scattering data, *Journal of Applied Crystallography* 10(5) (1977) 415-421.
- [3] R. Rameshan, A. Nenning, J. Raschhofer, L. Lindenthal, T. Ruh, H. Summerer, A.K. Opitz, T. Martin Huber, C. Rameshan, Novel Sample-Stage for Combined Near Ambient Pressure X-ray Photoelectron Spectroscopy, Catalytic Characterization and Electrochemical Impedance Spectroscopy, *Crystals* 10(10) (2020) 947.
- [4] D. Barreca, A. Gasparotto, C. Maccato, C. Maragno, E. Tondello, ZnO nanoplatelets obtained by chemical vapor deposition, studied by XPS, *Surface Science Spectra* 14(1) (2007) 19-26.
- [5] L. Dobrzański, L. Żukowska, J. Kubacki, K. Gołombek, J. Mikuła, XPS and AES analysis of PVD coatings, *Archives of Materials Science and Engineering* 32(2) (2008) 99-102.
- [6] R. Fu, N. Yoshizawa, M.S. Dresselhaus, G. Dresselhaus, J.H. Satcher, T.F. Baumann, XPS study of copper-doped carbon aerogels, *Langmuir* 18(26) (2002) 10100-10104.