A one pot hydrothermal synthesis of sulfur and nitrogen doped carbon aerogels with enhanced electrocatalytic activity in the oxygen reduction reaction – Electronic Supplementary information (ESI)

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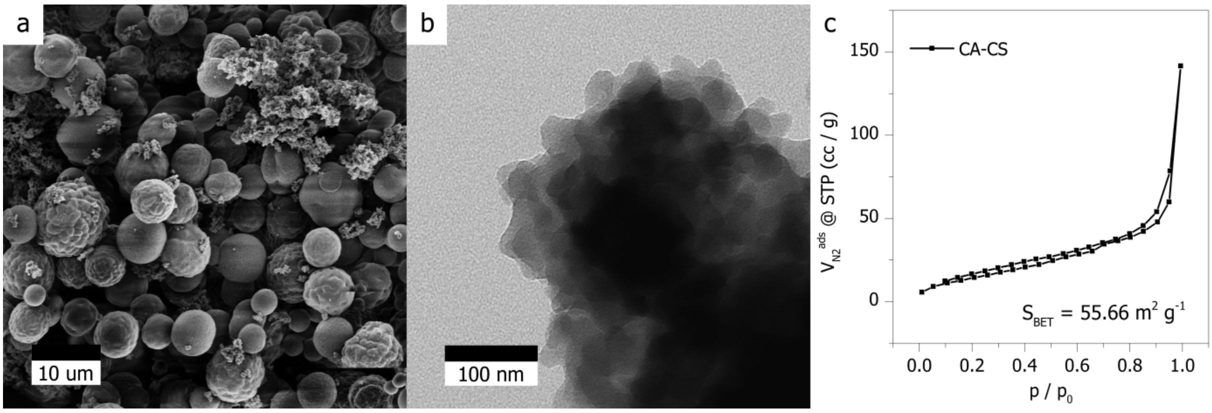
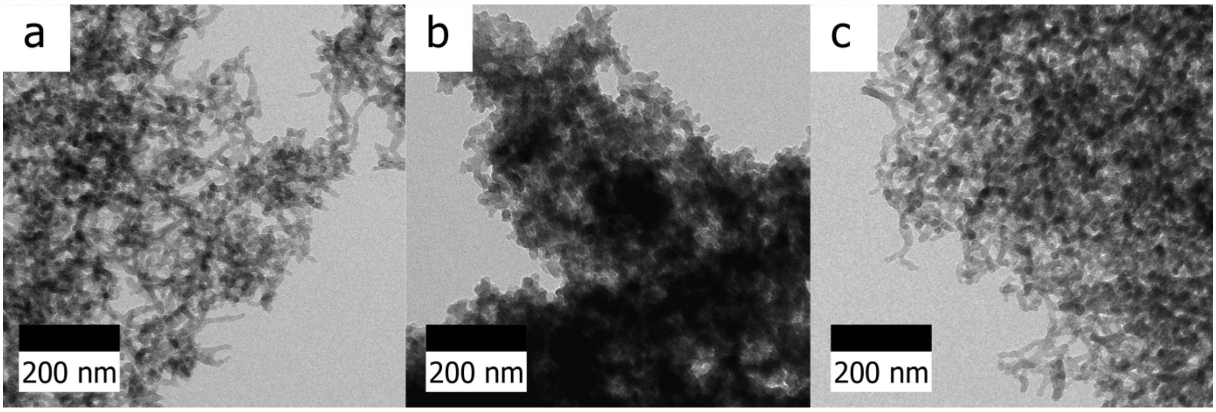
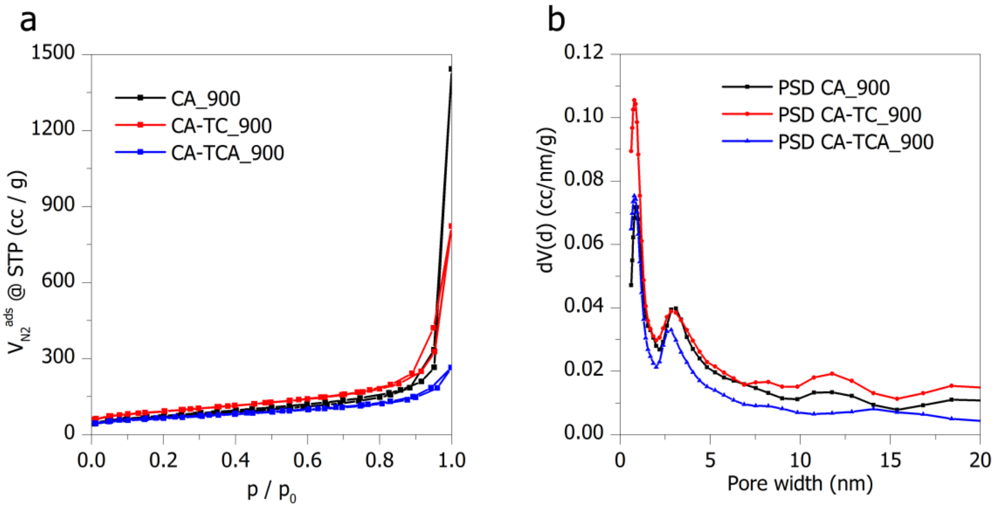


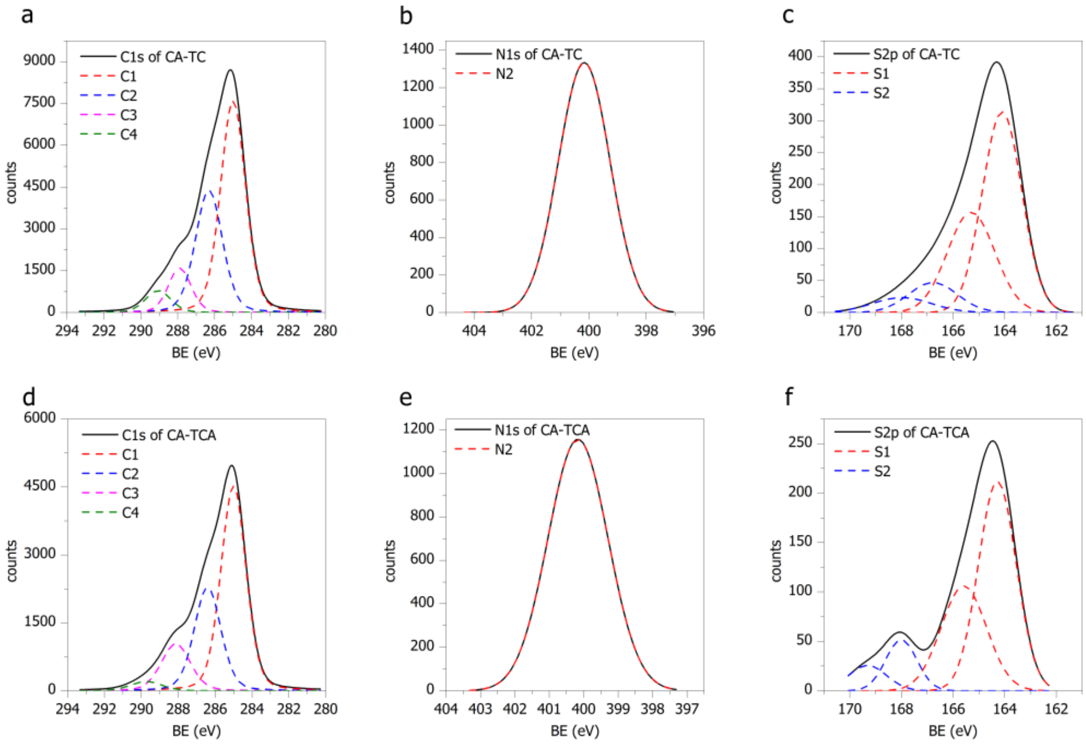
ESI Fig. S1 *Addition of cysteine to HTC of glucose and ovalbumin. A) SEM image, b) TEM image, and c) nitrogen sorption isotherm of the obtained product.*



ESI Fig. S2 *TEM images of a) CA_900, b) CA-TC_900, and c) CA-TCA_900*



ESI Fig. S3 *a) Nitrogen sorption isotherms and b) pore size distributions (QSDFT model) obtained for aerogels after HTC at 180 °C.*



ESI Fig. S4 *Deconvoluted C1(s) N1(s) and S2(p) photoelectron envelopes of CA-TC (a, b, c, respectively), and CA-TCA (d, e, f, respectively)*

Physical and Chemical Sample Characterization

N_2 sorption analysis was performed at 77 K using a QUADROSORB SI, equipped with automated surface area and pore size analyzer. Before analysis, samples were degassed at 60 °C (as-synthesized aerogels) or 150 °C (pyrolized aerogels) for 20 h using a "Masterprep" degassing system. Quenched Solid Density Functional Theory (QSDFT) pore size distributions (PSD) were calculated using, as this evaluation model takes into account the effects of surface roughness and chemical heterogeneity of the material surfaces.

Material morphology was visualized using a Gemini Scanning Electron Microscope (**SEM**). Transmission Electron Microscopy (***TEM***) was carried out with a Carl Zeiss Omega 912X at an acceleration voltage of 120 kV. Samples for High resolution transmission electron microscopy (**HRTEM**) were prepared by dry deposition of the material onto holey carbon copper grids. **Analytical TEM** was performed using a Philips CM 200 microscope with a field emission gun operated at 200kV. **XRD** patterns were recorded on a Bruker D8 diffractomenter over the 2θ range of 5 to 80° using Cuα radiation and a scan rate of 1 ° min^{-1}.

Elemental analysis was obtained on a Vario El elemental analyzer. **XPS analysis** of the samples was performed using a Thermo Scientific Kα ESCA instrument equipped with Al Kα1, 2 monochromatized radiation at 1486.6 eV X-ray source. Charge neutralization was performed by using both a low energy flood gun (0 to 14 eV) and a low energy Ar ion gun. The XPS measurements were carried out using monochromatic Al-Kα radiation (hν = 1486.6 eV). Photoelectrons were collected at 90° to the sample surface. A constant analyzer energy mode (CAE) with 100 eV pass energy for survey spectra and 20 eV pass energy for high resolution spectra was used. The spectra were calibrated by setting the C1s photo peak at 285.0 eV. For sulfur, the $S2p_{3/2}$ peak was used for the assignment of binding states. Surface elemental composition was determined using standard Schofield photoemission cross sections. Peak assignments were carried out by using the values reported in the NIST XPS Database iii and references indicated in the text. . **Specific conductivity measurements** were carried out with Gamry Reference 600/3000 potentiostat (Gamry Instruments) and Gamry EIS 300/Physical Electrochemistry software. Electrical conductivity was achieved applying R-model on potentiostatic impedance spectroscopy at 1-1000 Hz using a two electrode setup. To perform **electrochemical testing** a standard ink was prepared from ~5 mg of catalyst with 95 µl Nafion® binder solution and 350 µl of ethanol. The ink was ultrasonicated for at least 30 minutes for homogenization. A 5 µl aliquot was dropped onto a freshly polished glassy carbon rotating disk electrode (diameter ~ 5 mm, electrode area 0.196 cm²) to prepare a catalyst thin film. When necessary, the electrode was warmed to ~ 50 °C in an oven prior to ink application in order to achieve better electrode coverage of the catalyst film. Electrochemical tests were performed in 0.1 M KOH or 0.1 M $HClO_4$ in a standard three - electrode setup with an Ag / AgCl reference electrode using Gamry Reference 600 potentiostate (Gamry Instruments) and Gamry EIS 300/Physical Electrochemistry software. The obtained current values were normalized to the mass of the catalyst used (*i.e.* given in mA mg^{-1}) for direct comparison between samples. For **Koutecky-Levich analysis**, the un-normalized currents obtained from measurements at varying rotation rates (600, 1000, 1600, 2000, and 2600 rpm) were used.

The Levich current, $\mathbf{I_{lev}}$, is given by

$$I_{lev} = 0.62nFAD^{\frac{2}{3}}\omega^{\frac{1}{2}}\nu^{-\frac{1}{6}}C$$

where

n	number of electrons transferred in the half reaction
F	Faraday constant
A	electrode area
D	diffusion coefficient of the reactant in the electrolyte
ω	angular rotation rate of the electrode
ν	kinematic viscosity of the electrolyte
C	analyte concentration

The kinetic current, I_k is given by:

$$I_k = nFAkC\Gamma_{cat}$$

n	number of electrons transferred in the half reaction
F	Faraday constant
A	electrode area
k	pseudo second order rate constant
C	analyte concentration
Γ_{cat}	catalyst loading

Combining both equations leads to the Koutecky-Levich expression, which describes the overall RDE limiting current I_{lim} for the electrocatalytic reaction over the entire potential range:

$$\frac{1}{I_{lim}} = \frac{1}{I_k} + \frac{1}{I_{lev}}$$

A plot of $\frac{1}{I_{lim}}$ against $\frac{1}{\omega^{\frac{1}{2}}}$ should yield a straight line whose slope is related to the **number of electrons** transferred in the reaction, and whose intercept is related to the kinetic current.