**Nitrogen-doped coatings on carbon nanotubes and their stabilizing effect on supported Pt nanoparticles**

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**Supporting information**

**Synthesis of nitrogen doped carbon nanotubes**

3MBP-dca was acquired from VWR. CNTs were Baytubes purchased from the Bayer® company. Sulphuric acid was acquired from Sigma Aldrich. Ethanol was acquired from Carl Roth with a purity of ≥ 99.8%. The chemicals were entirely used without further treatment. Annealing of samples was accomplished in Nabertherm® box type furnaces, equipped with a continuous gas.

CNTs were pre-oxidised by dispersion in sulphuric acid (c = 2 mol l⁻¹) by sonication. After stirring the dispersion vigorously overnight the black residue was isolated by centrifugation, frequently washed with deionised water and subsequently dried overnight in the vacuum drying oven.

For the preparation of the coating the CNTs were dispersed in a 30 wt% solution of 3MBP-dca in deionised water by sonication. The resulting black slurry was filtered by vacuum filtration and the black residue in the filter was washed with 50 mL of ethanol to remove excess IL. The residue was subsequently placed in ceramic crucible and thermally treated in a furnace under constant argon flow to 1000 °C applying a heating rate of 100 K h⁻¹. After 1 h at 1000 °C the sample was allowed to cool down to room temperature and subsequently pestled for further use.

**XPS measurements**

The XPS-measurement was performed using a VG ESCALAB 200 X xp-spectrometer, manufactured by VG Scientific, East Grinstead, UK. Using this spectrometer, electron spectra were recorded using polychromatic Al-Kα excitation (15 kV, 20 mA) and an emission angle of 0 degree. The spectrometer energy scale was calibrated following ISO 15472 [1]. The survey scans were measured in constant retardation ratio (CRR) mode, while
narrow scans were done in constant analyser energy (CAE) 20 mode. In order to correct the binding energy scale for static charging, an electron binding energy of 285.0 eV [2] for the C 1s reference level of aliphatic hydrocarbon was used. The samples were fixed nonconductively on a double sided silicon free carbon tape. The analysis of XPS spectra was done with the Unifit 2011 software, developed by R. Hesse, Unifit Scientific Software GmbH, Leipzig, Germany. As fitting strategy for the peakformanalysis the convolution with a fully fitable Tougaard background correction was chosen [3,4]. The spectral parameters are shown in Table 1.

Tab. 1: Peak fit parameter of the N 1s detail spectrum in inset of fig. 1

<table>
<thead>
<tr>
<th>Peakname</th>
<th>graphitic N</th>
<th>pyridinic N</th>
<th>ox. N-species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian width / eV</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Lorentzian width / eV</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>Asymmetry α</td>
<td>0.09</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>binding energy / eV</td>
<td>401.1</td>
<td>398.7</td>
<td>404.0</td>
</tr>
<tr>
<td>rel. amount / %</td>
<td>61.8</td>
<td>35.7</td>
<td>2.5</td>
</tr>
<tr>
<td>total amount / at.-%</td>
<td>0.6</td>
<td>0.4</td>
<td>-</td>
</tr>
</tbody>
</table>

Nitrogen sorption measurements

Nitrogen sorption isotherms were measured using a Quadrasorb porosimetry device manufactured by Quantachrome, samples were degassed at 150°C for 20 h at reduced pressure before measurement.

Figure S1: Nitrogen-sorption isotherms of raw Baytubes, hydroxylated Baytubes and N/C-functionised Baytubes in comparison.

Synthesis of supported Pt-Nanoparticles

Nanoparticles were synthesized following the polyol process route. 5 mM of H₂PtCl₄ was dissolved in 50 ml of a 15 mM NaOH-ethyleneglycol solution. The solution was heated to 160°C with reflux under nitrogen atmosphere. The temperature was kept constant at 160°C for 20 minutes. Color change of the solution from yellow to dark brown indicated the formation of the nanoparticles. The reaction solution was cooled down immediately using a water bath. Support material was dispersed in 80 ml of a 2 M sulfuric acid and sonicated for 10 minutes. The as
prepared Pt-NP solution was added to the support solution and stirred for 24 hours. The solvents were removed by centrifugation (7700 rounds per minute). The powders were washed 3 times with water and freeze-dried afterwards. For synthesis and for each following procedures Millipore® ultra pure water was used.

**ICP-OES sample preparation**

The weight loading of Pt-NP was determined using the optical emission spectroscopy with inductive coupled plasma as ionization source (ICP-OES). For the spectroscopical measurements ~ 5 mg of a dry powder was dissolved in 10 ml mixture of sulfuric (2 ml), nitric (2 ml) and chloric (6 ml) acids. The solution degassed in a fume hood overnight and was then exposed to microwaves to heat up to 180°C in 10 min with a constant heat gradient. The temperature was held for 20 min whereas the gas pressure was controlled to not exceed 18 bar. The solution was filtered to remove the remained carbon, diluted to 3 different concentrations and analyzed with ICP-OES Varian 715-ES. The amount of dissolved Pt was determined using the standard calibration method.

**XRD analysis and results**

Diffraction patterns were collected with a Bruker D8 Advance Diffractometer (40 mA, 40 kV). The size of crystalline particles was calculated from the background-corrected patterns of pristine powders using the Scherrer equation for each peak obtained from fits, which overlaid with the reflections of Pt (figure S1a for Pt-NP on CNTs and S1b for Pt-NP on N-CNTs). These values are attended by the previously obtained information on particle size from TEM and SAXS.

![Figure S2: Diffraction patterns (black) and corresponding fits (colored) for each Pt powder diffraction file overlaid peak for 20 wt% Pt on CNTs (a) and for 17 wt% Pt on N-doped CNTs (b).](image-url)
TEM analysis

For TEM sample preparation a small amount of the synthesized powder was dispersed via ultra sonification in 0.5 ml of iPrOH. A Cu-grid with holey carbon film was impregnated with 2 μl of the solution and air-dried. The FEI TECNAI G² 20 S-TWIN microscope, equipped with a GATAN MS794 P CCD-detector, was operated by the accelerating voltage of 200 kV.

Electrochemical protocols and characterization

For electrochemical measurements inks of the synthesized powders were prepared as following: Approximately 5 mg of the powder was dispersed in a mixture of 2490 μl of water, 2490 μl iso-propanol and 20 μl of a 5% wt Nafion solution in iso-propanol. The mixture was ultra sonicated with an output power of 6 W for 15 minutes.

The measurements were performed using a PINE glassy carbon (GC) rotating disk electrodes. The electrodes were polished in two steps: first with Buehler Alpha micropolish 1 solution on a Nylon sheet and second after rinsing with ultrapure water with Buehler Alpha micropolish 0.05 solution on a Microloth® sheet. Electrodes were then sonicated in water, in acetone and in water again, each procedure for 5 minutes, to remove the polishing solution rests. The as prepared electrodes were coated with 15 μl of an ink solution and air dried.

Electrochemical characterization was performed with a Biostat SP-200 in 0.1 M HClO₄, saturated with N₂ for cyclic voltammetry (CV) and O₂ for linear sweep voltammetry (LSV). ECSA was determined from CV (0.005 – 1.100 V, 50 mVs⁻¹) in a range of 0.005 – 0.400 V. Specific activity of the catalyst for the oxygen reduction reaction was determined at 0.9 V from LSV (0.060 – 1.020 V, 5 mVs⁻¹) by factoring the geometric area of the glassy carbon disk (0.196 cm²). A potential steps protocol is showed in detail in table 2.

Table 2: Detailed electrochemical protocol applied on Pt-NP on CNTs and on N-CNTs for electrochemical characterization and degradation study.

<table>
<thead>
<tr>
<th>Technique</th>
<th>( H_{\text{upd-CV}} )</th>
<th>Activation-CV</th>
<th>( H_{\text{upd-CV}} )</th>
<th>LSV</th>
<th>AST-CV</th>
<th>( H_{\text{upd-CV}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of cycles</td>
<td>3</td>
<td>200</td>
<td>3</td>
<td>0.5</td>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td>Range / V</td>
<td>0.005-1.100</td>
<td>0.005-1.100</td>
<td>0.005-1.100</td>
<td>0.06-1.020</td>
<td>0.500-1.100</td>
<td>0.005-1.100</td>
</tr>
<tr>
<td>Scanrate / mVs⁻¹</td>
<td>50</td>
<td>500</td>
<td>50</td>
<td>5</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Loop for 24 times
Small angle x-ray scattering data analysis

SAXS data were collected with a Bruker AXS NanoStar lab system, operated with a rotating Cu-target anode at 45 kV and 110 mA. The scattered x-rays of a Cu-Kα wavelength (0.154 nm) were detected with a 2D HiStar photon counting detector. Scattering patterns of pristine powders were collected for 300 s, those of the in-situ experiments for 600 s. For background correction SAXS patterns from CNTs and N-CNTs were used, treated the same way as described above in a section synthesis of supported Pt-Nanoparticles in an absence of Pt-precursor in the solution. Background patterns for in-situ measurements were obtained from electrodes impregnated with an ink of treated CNTs and N-CNTs. The ink preparation is described in the section electrochemical protocols and characterization. Carbon sheet electrodes (175 µm thick, Fuel cell store) were impregnated 10 times with 10 µl of an ink to maximize the amount of Pt nanoparticles in the x-ray spot. In table 3 the applied electrochemical protocol is described.

Table 3: Detailed electrochemical protocol applied on Pt-NP on CNTs and on N-CNTs for in situ SAXS measurements

<table>
<thead>
<tr>
<th>Technique</th>
<th>Chrono-amperometry, 10 min SAXS measurement</th>
<th>Activation-CV</th>
<th>Chrono-amperometry, 10 min SAXS measurement</th>
<th>AST-CV</th>
<th>Chrono-amperometry 10 min SAXS measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of cycles</td>
<td>-</td>
<td>200</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Range / V</td>
<td>0.500</td>
<td>0.005-1.100</td>
<td>0.500</td>
<td>0.500-1.100</td>
<td>0.500</td>
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<tr>
<td>Scanrate / mVs⁻¹</td>
<td>-</td>
<td>500</td>
<td>-</td>
<td>50</td>
<td>-</td>
</tr>
</tbody>
</table>

Loop for 24 times

Raw SAXS 2D patterns were integrated in the Chi range of -180° to 180° and a 2θ range of 0.1° – 5.0° with a step size of 0.01. The resulting 1D scattering curves are a function of intensity dependent on the scattering vector \( \tilde{q} \), defined as:

\[
\tilde{q} = \text{wave}_{\text{out}} - \text{wave}_{\text{in}};
\]

\[
|\tilde{q}| = q = \frac{2\pi}{\lambda} \sin 2\theta. \tag{1}
\]

Here \( \lambda \) is a wavelength of the x-ray, 2θ is the angle of the scattered wave relative to the incident wave. Scattering curves were normalized by transmission. An additional scattering measurement of a sample with a GC plate, placed between the sample and the detector, gave the required information on sample transmission:

\[
I_{\text{sample, corrected}} (q) = \frac{I_{\text{sample}} (q)}{I_{\text{sample}} + GC - \tau_{GC} \cdot I_{\text{sample}}}. \tag{2}
\]
Here \( q \) is the scattering vector, \( I(q) \) the intensity function obtained from the integration of the SAXS pattern, \( \tau_{GC} \) the transmission of the GC plate, \( I \) is the number of the detected counts per second of the measurement with and without a GC plate. For background correction transmission corrected blank sample curves were subtracted from transmission corrected particle containing scattering curves. Resulting corrected scattering curves were fitted using the SASfit 0.93.2 software. A Lognormal size distribution of spherical particles was assumed. Hence, the fit function is represented by eq. 3, where the LogNormal distribution is defined by eq. 4 and the form factor of a single hard sphere by eq. 5:

\[
I_{fit}(q,R) = \text{scale} \cdot \text{LogNorm}(R;\sigma,\mu)P(q,R);
\]

\[
\text{LogNorm}(R;\sigma,\mu) = \frac{N}{\sqrt{2\pi}\sigma} \frac{1}{R} \exp \left( -\frac{(\ln R - \mu)^2}{2\sigma^2} \right);
\]

\[
P(q,R) = \frac{3V(\Delta \rho)(\sin(qR) - qR \cos(qR))}{(qR)^3}.
\]

Here \( q \) is the scattering vector, \( R \) is a radius of a single hard sphere, \( \mu = \ln R_{median} \) is related to the median sphere radius of polydisperse particles, \( \sigma \) is the standard deviation of the distribution, \( N \) is the particle number density and \( \Delta \rho \) is the the scattering length density. The \( n^{th} \) moment of the LogNormal distribution is given by:

\[
\langle R^n \rangle = \exp(n \cdot \mu + n^2\sigma^2/2).
\]

The mean radius is the first moment of the LogNormal distribution. A more precise determination of the exact particle radius \( R_{lc} \) can be calculated using a correlation length \( l_c \). This parameter was introduced by Porod [6] and is specified by the region, where the correlation function differs from 0. It can be expressed in terms of the moments of the distribution. Hence, in our study we use the more precise value \( R_{lc} \):

\[
R_{lc} = \frac{2}{3} l_c = \frac{\langle R^4 \rangle}{\langle R^3 \rangle}.
\]

The evaluation of an overall value of particle size that is plotted in figure 3 is performed using a number density normalization as following:

\[
\text{size}_{all} = \frac{\text{size}_1 \cdot N_1 + \text{size}_2 \cdot N_2}{N_1 + N_2}
\]
Figure S3: LSV for specific activity calculation (O2-saturated 0.1 M HClO4, 0.06 – 1.0 V, 5 mVs-1), CVs for Hupd calculation (O2-saturated 0.1 M HClO4, 0.005 – 1.1 V, 50 mVs-1) and in-situ monitored SAXS curves (dots) with corresponding fits (lines) for 20 wt% Pt on CNTs (a, b and c) and for 17 wt% Pt on N-CNTs (d, e and f). SAXS curves in c) and f) are divided by a factor for more clearance in the plot.

References


