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Tailoring the Oxygen Reduction Activity of Pt Nanoparticles through Surface Defects: A Simple Top-Down Approach

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4 **KEYWORDS:** Electrocatalysis, Fuel Cell, Oxygen Reduction, Platinum Nanoparticles, Top-Down
5 Synthesis
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8
9 **ABSTRACT**
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12 Results from Pt model catalyst surfaces have demonstrated that surface defects, in
13 particular surface concavities, can improve the oxygen reduction reaction (ORR) kinetics.
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17 It is, however, a challenging task to synthesize nanostructured catalysts with such
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19 defective surfaces. Hence, we present a one-step and up-scalable top-down approach to
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21 produce Pt/C catalyst (with ~3 nm Pt nanoparticle diameter). Using high-resolution
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23 transmission electron microscopy and tomography, electrochemical techniques, high
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25 energy X-ray measurements and positron annihilation spectroscopy, we provide evidence
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27 of a high density of surface defects (including surface concavities). The ORR activity of
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29 the developed catalyst exceeds that of commercial Pt/C catalyst, at least 2.7-times in
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31 terms of specific (~1.62 mA/cm²_{Pt} at 0.9 V vs the reversible hydrogen electrode) and at
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33 least 1.7-times in terms of mass activity (~712 mA/mg_{Pt}), which can be correlated to the
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35 enhanced amount of surface defects. Besides, the technique used here reduces the
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3 complexity of the synthesis (and therefore production costs) compared to state-of-the-art
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7 bottom-up techniques.
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13 **Introduction**

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17 With the increased awareness of preventing the climate change, efforts are made to
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21 decouple our society's energy demands from the so-called carbon cycle. One promising
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24 approach is to reduce emissions caused by automotive combustion engines, for instance
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28 by replacing this technology with electric motors that are powered by either batteries
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31 and/or hydrogen fuel cells.^{1,2} Even though the market launch of hydrogen fuel cell driven
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34 cars is on the rise, further cost reductions are required to make the technology
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38 commercially more competitive. Today, anode and cathode catalyst layer of proton
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41 exchange membrane fuel cells (PEMFCs) typically consist of Pt-based nanostructures
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45 supported on high surface area carbon (Pt/C).³ While the hydrogen oxidation reaction
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48 taking place at the anode side of the cell is a rapid process, the oxygen reduction reaction
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51 (ORR) at the cathode side exhibits sluggish kinetics. In order to improve the activity of
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55 such catalysts, two approaches are typically pursued. One way is to alloy Pt nanoparticles
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4 with less precious transition metal elements (*e.g.*, Co, Ni, Cu) or lanthanides (*e.g.*,
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6 Pr),^{4,5,6,7} which alters the electronic properties of the catalyst surface by a combination of
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10 so-called “strain” and “ligand” effects. This weakens the strong surface-intermediate
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14 interactions and allows to optimize electron transfer.^{8,9} In particular, both Pt₃Ni bulk and
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18 nanoscale alloy structures notably exceeded the activity of pure Pt.^{10,11,12} However, due
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21 to the dissolution of the solute metal during PEMFC operation (commonly known as
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24 “dealloying”), the membrane electrode assembly can get poisoned, resulting in poor long
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28 term performance.¹³ Another promising approach is to directly alter the catalytic
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31 properties of Pt nanoparticles by the modification of their surface structure. Exemplary,
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35 tailoring the size of the nanoparticles and the design of unusual catalyst shapes with
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38 enhanced surface area (*e.g.*, hollow nanoparticles, aerogels) can be mentioned.^{14,15,16}
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42 Importantly, in such cases the increased activity towards the ORR can, amongst others,
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46 also be attributed to the generation of highly active defect-like surface sites. In particular,
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49 Calle-Vallejo *et al.* demonstrated that surface concavities on Pt significantly improve ORR
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52 kinetics.^{17,18} This is due to the optimized geometric structure at the concave sites, as
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56 quantified by the so-called generalized coordination number (\overline{CN}) approach. Particularly
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3 high \overline{CN} values have been predicted for *e.g.*, hollow or coalescing nanoparticles at their
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7 boundary, confirming aforementioned experimental findings. Furthermore, the activity of
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10 concave-shaped nanocubes was experimentally demonstrated by Yu *et al.*,¹⁹ but the
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13 degree of negative curvature was not very pronounced and the size of the concave
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17 nanocubes was larger than 20 nm, which results in low mass activity. Furthermore,
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21 development of a simple production method for such concave nanoparticles often is a
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24 non-trivial endeavor. Current research mainly focuses on the synthesis of such catalysts
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28 using conventional bottom-up techniques, which typically suffer from complex and time-
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31 consuming multiple-step procedures.²⁰ Hence, the development of a facile synthetic
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34 method for Pt nanostructures, which contain these active sites, is a crucial step towards
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38 the commercial realization of PEMFC-driven cars on a large scale. Here, we take
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42 advantage of a novel top-down synthetic route, in order to prepare Pt/C catalysts with a
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45 high degree of surface defects. This top-down approach, which was initially discovered
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49 decades prior to the beginnings of nanotechnology and introduced as atomization of
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52 metal cathodes,²¹ uses high alternating anodic and cathodic biases applied to metal wires
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56 immersed in an alkaline electrolyte, in order to produce nanoparticles at the electrode
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3 surface and subsequently release them into the electrolyte. Fundamental experiments on
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7 the nanoparticle synthesis by this approach were provided by Koper's, Li's and
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10 Bandarenka's groups in recent years and extended to different types of noble and non-
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13 noble metals as well as alloys and oxide materials.^{22,23,24,25,26} With the help of high-
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17 resolution transmission electron microscopy (HR-TEM), high-resolution scanning
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21 transmission electron microscopy with a high-angle annular detector (HR-STEM-
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24 HAADF), STEM-HAADF tomography visualization, Rietveld refinement of wide-angle X-
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27 ray scattering (WAXS), electrochemical techniques and positron annihilation
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31 spectroscopy (PAS), we provide evidence that the top-down synthesis leads to the
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34 formation of Pt nanoparticles with rough, disordered surfaces. In particular, this includes
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38 surface concavities. Furthermore, utilizing the rotating disk electrode (RDE) technique
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42 and single-cell PEMFC measurements, we show that Pt/C produced by this top-down
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45 approach (denoted as Pt/C_{TD} in the following) is indeed highly active towards the ORR.
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51 **Experimental Section**

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4 **Synthesis:** In a typical synthesis of Pt/C_{TD}, 20 mg of Vulcan XC72R active carbon (Cabot,
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7 USA) were dispersed in 25 ml of a 1 M KOH (85%, Grüssing, Germany) solution. To
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9
10 improve the wettability of the carbon support, ~100 µl of ethanol (puriss, >99.8%, Sigma
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13 Aldrich, Germany) were added to the suspension, followed by sonication for 15 min.
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17 Subsequently, two Pt wires (99,999%, Goodfellow, Germany) with a diameter of ~0.2 mm
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21 were connected as electrodes and immersed in the suspension under vigorous stirring.
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24 To produce Pt nanoparticles, a sinusoidal potential of ±10 V vs Pt pseudo-reference
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27 (frequency: 200 Hz) was applied, leading to the erosion of the Pt wires. After generation
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31 of the demanded Pt weight fraction, the suspension was stirred for 12h at room
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34 temperature, followed by filtering, washing with ultrapure water (Evoqua, Germany) and
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37 drying in the oven at 60°C. As a reference catalyst, TEC10V20E Pt/C (19.6 wt.%) from
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39
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41 Tanaka Kikinzoku Kogyo (Pt/C_{TKK}) was used without further modification.
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46 **Pt on carbon weight loading:** The weight fraction of Pt_{TD} nanoparticles on carbon was
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49 determined using TGA. The measurements were carried out with a METTLER TOLEDO
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53 TG-MS coupling instrument with an air flow of 50 ml/min and heating speed of 50 K/min
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3 to 1100°C. Prior to ramping the temperature, the sample was dried at ~135°C, followed
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7 by determination of its initial weight. Before cooling down, the sample was kept at 1100°C
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10 for 50 minutes until no further weight loss could be observed. The mass was compared
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14 after cooling down to 135°C.
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18 **Electron microscopy:** For TEM imaging of the Pt/C_{TD} electrocatalyst, a Philips CM100 EM,
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21 operated at 100 kV, was used. The samples were prepared by sonicating the catalyst
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24 powder in isopropanol, followed by drop-casting the dispersion on formvar-supported
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27 carbon-coated Cu400 TEM grids (Science Services, Germany). HR-(S)TEM imaging of
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29 the unsupported Pt_{TD} nanoparticles was conducted on a TITAN Themis 60-300
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32 (ThermoFisher Scientific, USA) operated at 300 kV and equipped with a Schottky FEG
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35 type emission gun, a spherical aberration corrector for the objective lens and HAADF
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38 detector (Fischione, USA). The TEM sample of the unsupported Pt_{TD} nanoparticles was
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41 prepared from Pt nanoparticles dispersed in ultrapure water by sonication for 15 minutes,
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44 which were immediately dripped on a copper TEM grid with quantifoil holey carbon
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47 membrane covered by graphene oxide. The HR-TEM and HR-STEM images were
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4 acquired using the software Velox v.2.6 (ThermoFisher Scientific, USA) and Fourier
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7 filtering was performed using masks on selected spots in fast Fourier transformation
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10 (FFT) patterns in the software Digital Micrograph GSM 2 (Gatan Inc., USA). The
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13 tomography of the unsupported Pt_{TD} nanoparticles was conducted on a TITAN 80-300
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16 (FEI company, USA) operated at 300 kV in STEM mode using the HAADF detector, which
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19 allows imaging with high contrast between Pt nanoparticles and the carbon membrane of
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22 the TEM grid. The same sample as for TEM analysis (described above) was used, but
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25 round Au tracking nanoparticles with ~6.5 nm in size, dissolved in high-purity water, were
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28 dripped on the grid additionally to allow later alignment of the images in the whole tilting
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31 range. The used tilting range was +/-72° and the STEM-HAADF images were taken in 2°
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34 steps. A 2020 high field-of-view single-tilt tomography holder (Fishione, USA) was used
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37 for the tomography tilt series acquisition. The tomography data were obtained using the
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40 corresponding STEM tomography data acquisition software v.4.1 (ThermoFisher
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43 Scientific, USA) with automatic and dynamic focusing. The post processing of the
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46 tomography data consisted of three parts: alignment, reconstruction and visualization.
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56 The alignment was performed using the open-source software IMOD v.4 (University of
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3 Colorado, USA) with plugin eTomo, where a fiducial model was created by manual
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6 tracking of Au beads surrounding the structure of interest with a residual error of the
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9 alignment of 1.2 pixel. The reconstruction was performed using the software Inspect3D
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12 v.3.1 (FEI company, USA) from the previously aligned dataset and a 3D volume of the
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15 desired size was created. The final colorful visualization of reconstructed volume was
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18 performed using the software AMIRA (ThermoFisher Scientific, USA).
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25 **Electrochemical measurements:** Electrocatalytic activity measurements were performed
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28 using a standard electrochemical cell, filled with 0.1 M HClO₄ (Suprapur®, Merck,
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31 Germany) as electrolyte. The cell was frequently cleaned with a 3:1 ratio of sulfuric acid
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34 and hydrogen peroxide, followed by boiling the cell with ultrapure water. Electrochemical
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37 measurements were conducted using a BioLogic VSP-300 (BioLogic, France)
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39
40 potentiostat. As a substrate for Pt/C_{TD}, a glassy carbon electrode with a diameter of 5 mm
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43 and an area of 0.196 cm² (Pine instruments, USA) in combination with a Pine MSR
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46 electrode rotator (Pine instruments, USA) was used. For electrochemical studies, freshly
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49 prepared catalyst inks were used. A typical catalyst ink ratio consisted of ~10 mg finely
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4 grinded catalyst powder, 3.6 ml of ultrapure water, 1.466 ml of isopropanol (puriss.,
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7 >99.8%, Sigma Aldrich, Germany) and 0.03 ml of Nafion dispersion (5 wt.% in lower
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10 aliphatic alcohols and water, Sigma Aldrich, Germany). To obtain a homogeneous
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13 dispersion, the inks were sonicated for 20 minutes prior to their first use. Prior to usage,
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16 the electrode was polished with alumina paste (1.0, 0.3, and 0.05 μm) and rinsed with
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19 ultrapure water. A commercial mercury/ mercurous sulfate electrode (Schott, Germany)
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22 served as reference electrode. A Pt wire (99.9%, Goodfellow, Germany) served as
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25 counter electrode. It has to be noted that CO-stripping voltammetry was recorded in a
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28 slightly modified setup. As a reference electrode, a commercial Hydroflex® hydrogen
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31 electrode (Gaskatel, Germany) was utilized. Experiments were operated with an Autolab
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38 PGSTAT302N potentiostat (Metrohm, France).
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47 **Membrane electrode assembly measurements:**

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51 Single-cell PEMFC measurements were conducted in a home-made cell setup. Fuel cell
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53 performance was evaluated on a Greenlight Innovation G60 test station (Greenlight Innovation
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3 Corp., Canada), coupled with a Gamry reference 3000 potentiostat (Gamry Instruments, USA). 5
4 cm² catalyst layers were prepared using the decal transfer method, *i.e.*, by rod coating on a PTFE
5 decal, followed by drying at room temperature. As anode catalyst, commercial Pt/C_{TKK}
6 (TEC10V20E) with an anode loading of 0.08 mg_{Pt}/cm² was used. As cathode catalyst, Pt/C_{TD} with
7 a cathode loading of 0.1 mg_{Pt}/cm² was utilized. Synthesis of Pt/C_{TD} electrocatalyst was conducted
8 as described in the previous sections, however, the batch size was increased from ~20 mg to ~100
9 mg of Pt/C_{TD}. For ink preparation, the catalyst was dispersed in a mixture of 1-propanol and water
10 (~10 wt%) and an ionomer (Nafion, 5%_{w/w} in lower aliphatic alcohols and water, Sigma Aldrich,
11 Germany) to carbon (I/C) ratio of 0.65 was adjusted. The ink was mixed on a roller mill for 18 h
12 at room temperature, using ZrO₂ beads. Anode, 15 μm membrane and cathode were hot-pressed
13 for 3 min at 155°C and 4 kN. A Freudenberg H14C7 (Freudenberg & Co. KG, Germany) served
14 as the gas diffusion layer. To record CO-stripping voltammograms, the cell was purged with 10%
15 CO in N₂ for ~10 min at a constant potential of 0.1 V, followed by purging with pure N₂ to remove
16 excess of CO. The voltammograms were recorded at a scan rate of 100 mV/s. Differential flow
17 H₂/O₂ (2000 nccm/5000 nccm) polarization curves were recorded at 80°C, 170 kPa_{abs} and 100%
18 relative humidity. The ohmic resistance was determined via electrochemical impedance
19 spectroscopy. The H₂ crossover was determined in H₂/N₂ atmosphere.
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43 **Positron annihilation spectroscopy:** For the present study, coincident Doppler broadening
44 spectroscopy (CDBS) was performed at the CDB spectrometer using the mono-energetic
45 positron beam at NEPOMUC located at the research neutron source Heinz Maier-Leibnitz
46 (FRM II).²⁷ The positron implantation energy was varied between 0.10 and 30 keV.^{28,29} In
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3 order to examine the near surface region, small energy steps of 0.10 and 0.20 keV were
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7 chosen up to an implantation energy of 8 keV. The energy of the emitted annihilation
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10 radiation was recorded by high-purity Ge detectors with a typical energy resolution of 1.30
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13 keV at 511 keV. For the calculation of the S -parameter the central energy interval was
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16 set to (511 ± 0.85) keV. The CDB spectra were recorded at a positron implantation energy
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19 of 0.4 keV where the contribution of the Si substrate can be neglected according to the
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21
22 calculated Makhov profile. Preparation of the samples was performed by dispersing 10
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25 mg of Pt/C_{TD} and commercial Pt/C_{TKK} catalyst powder in 1 ml of ethanol via sonication.
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31 The as-prepared inks were drop-casted onto a silicon wafer, followed by drying of the
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34 sample at 60°C for 1 h.
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39 **WAXS measurements and Rietveld refinement:** WAXS patterns of Pt/C_{TD} and the
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42 commercial Pt/C_{TKK} were measured at the ID31 beamline of the European synchrotron
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45 radiation facility (ESRF, Grenoble, France). High energy X-ray radiations of 70 keV were
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48 focused on the catalyst powder contained either in a Kapton® tape (powder film removed
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51 from a rotating disk electrode) or Kapton® capillary for Pt/C_{TD} and commercial Pt/C_{TKK},
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3 respectively. The scattered signal was collected using a Dectris Pilatus CdTe 2M detector
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6 within 5 s exposure time. The 2D signal was azimuthally integrated and reduced to a 1D
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9 curve using the pyFAI software package after the energy,³⁰ detector distance and tilt were
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12 calibrated using a standard CeO₂ powder. The lattice parameter, crystallite size and
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15 microstrain values for the electrocatalysts were estimated by Rietveld refinement of the
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17
18 WAXS patterns using an *Fm3m* structure of metallic Pt and the Fullprof software.³¹ Due
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20
21 to an external pollution by Ni, an additional Ni phase was added to refine Pt/C_{TD}. The
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24 instrument resolution function was determined from the CeO₂ standard WAXS pattern,
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26
27 the peak shape and the background were described using the Thompson-Cox-Hastings
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30 (TCH) function and by a polynomial function, respectively. A possibility for uniaxial
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33 anisotropic description of nanoparticle size along the [111] direction axis was also
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36 implemented.
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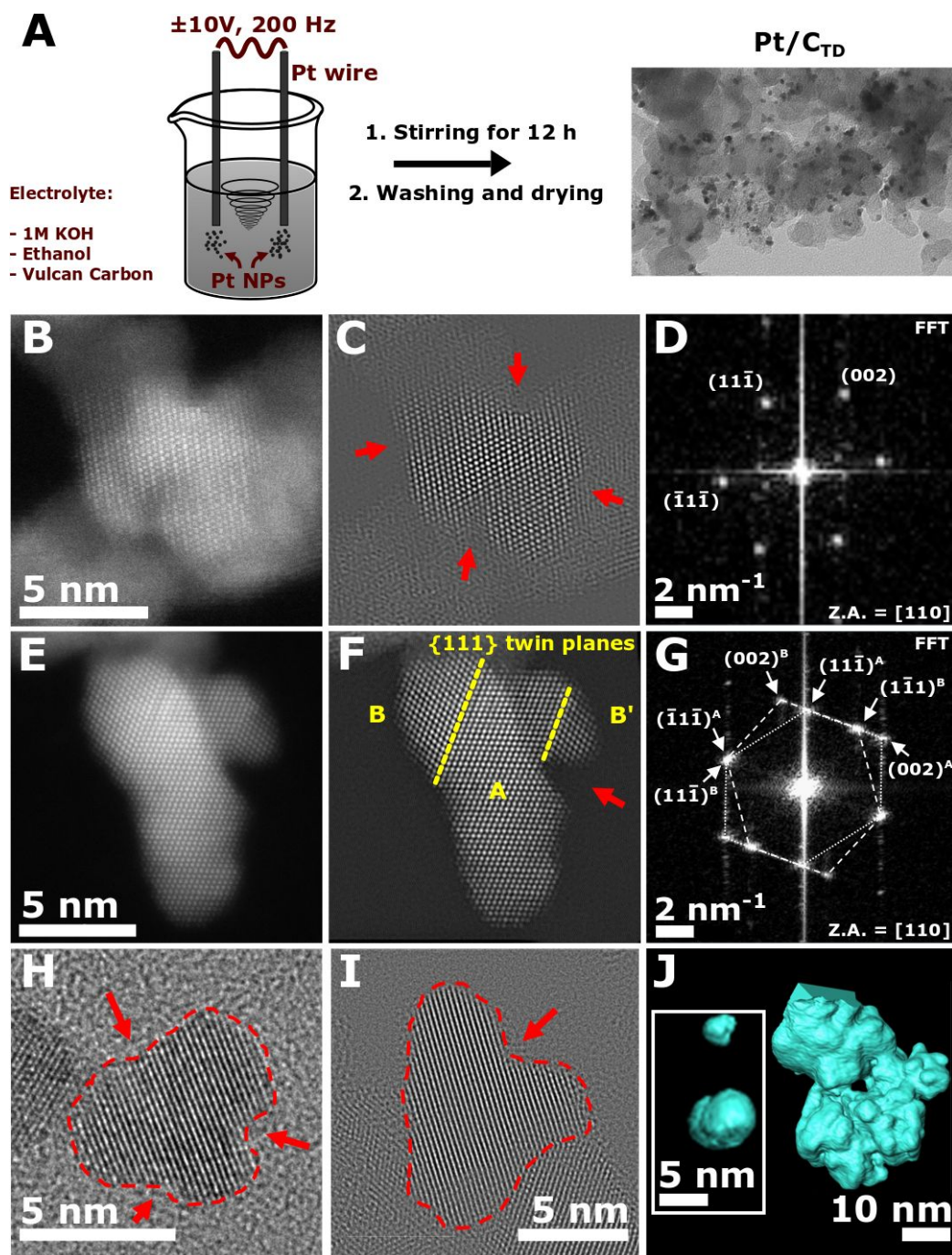
47 **Results and Discussion**

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50 During the top-down synthesis process (see Figure 1A), Pt wires are exposed to strongly
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53 polarizing, alternating voltages. Thereby, nanoparticles can be rapidly eroded from the
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3 wire surface and subsequently be released into the electrolyte. Due to the rough
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6 conditions of our synthetic route, we assume to produce a wide variety of nanoparticle
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9 shapes, including surface concavities, combined with the introduction of local strain. In
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12 order to investigate the surface-defective character of Pt/C_{TD}, five different approaches
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15 were exploited:
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22 1. HR-(S)TEM was used to visualize certain defective surface sites of unsupported
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25 Pt_{TD} nanoparticles.
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32 2. STEM-HAADF tomography visualization was performed to obtain 3D information
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35 about the disordered surface regions of unsupported Pt_{TD} nanoparticles.
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42 3. PAS was employed to compare the defect concentration of Pt/C_{TD} to commercial
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45 Pt/C_{TKK} (detailed information about the reference catalyst is given in the
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48 experimental section).
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55 4. Rietveld refinement of WAXS measurements was performed to investigate and
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58 quantitatively compare the defect-induced degree of microstrain of Pt/C_{TD} to
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60 commercial Pt/C_{TKK}.

5. Electroanalytical methods were used to monitor and compare structural defects and activities of both samples.



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4 **Figure 1.** (A) Schematic description of the synthetic procedure towards Pt/C_{TD}
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7 electrocatalyst. Application of an alternating sinusoidal potential ($\pm 10V$, 200 Hz) to Pt
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10 wires immersed in a suspension of Vulcan carbon in 1 M KOH and ethanol under
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13 vigorous stirring leads to the formation of carbon supported Pt nanoparticles. (B,E) HR-
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16 STEM images of unsupported Pt_{TD} single nanoparticles with corresponding (C,F)
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19 Fourier filtered images and (D,G) FFT patterns (Z.A. = zonal axis). Certain concavities
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22 are highlighted by red arrows. Twin boundaries and twin grains A, B, B' are marked in
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27 (F). (H,I) HR-TEM images of unsupported Pt_{TD} nanoparticles. Concave regions are
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30 highlighted by red arrows. (J) 3D visualization of two unsupported, single Pt_{TD}
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33 nanoparticles, as well as a fraction of unsupported nanoparticle agglomerate, using
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In Figure 1B–I, unsupported Pt single nanoparticles are characterized with use of HR-
TEM and HR-STEM imaging. The images reveal a non-spherical structure of the

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3 nanoparticles produced. Indeed, several concave-shaped surface regions can be found,
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7 as exemplary highlighted by red arrows. In detail, several complex shapes of the
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10 nanoparticles were found, as it is demonstrated by two nanoparticles imaged by HR-
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12
13 STEM-HAADF technique in Figure 1B and E, where smaller concavities in the order of
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16 few crystal lattice planes and a sharp, deep concavity were revealed. These defects are
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19 highlighted in Figure 1C and F, respectively, where a Fourier filtering was used to reduce
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21
22 noise in original HR-STEM images to improve visibility of the atomic structure details. FFT
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25 patterns of both nanoparticles (Figure 1D and G), which were obtained from the original
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27
28 HR-STEM images, show spots corresponding to platinum {111} and {002} lattice planes
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31 with spacing of 0.227 nm and 0.196 nm, respectively,³² and crystal orientation of the
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34 nanoparticles to zone axis [110] of the face-centered cubic (FCC) lattice. The nanoparticle
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37 in Figure 1B was found to be a pure single crystal, while in the case of the nanoparticle
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40 in Figure 1E a twinned structure was revealed by FFT. The FFT in Figure 1G shows two
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43 [110] FCC zone axis patterns (marked by lattice indexes “A” and “B” and by dotted and
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46 dashed lines), which are rotated with respect to each other around the common {111}
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49 twin plane. Hand to hand to this finding, twinning of the nanoparticle by two corresponding
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4 planes of the {111} type was identified, which divides the crystal into three twin grains A,
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7 B and B', as it is marked in Figure 1F. In addition, the complex shape of the nanoparticles
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10 can be seen from a variation in contrast within both crystals imaged by the HR-STEM-
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13 HAADF technique in Figure 1B and E. The resulting contrast at the used imaging
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16 conditions is predominantly dependent on atomic number Z and thickness of the
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19 sample.³³ As the studied nanoparticles are pure Pt crystals, the contrast variations must
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22 originate from variations of the sample thickness. Therefore, it is also possible to
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25 demonstrate the topological complexity of both nanoparticles. Figure 1H and I show HR-
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28 TEM images of two Pt nanoparticles with "strawberry"-like shape, including up to three
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31 concave surface regions, which can be considered particularly interesting for
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34 electrocatalytic applications. To judge the complexity of the nanoparticle shapes in
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37 broader view, a state-of-the-art STEM-HAADF tomography technique, utilized for the
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40 visualization of complex 3D samples with high lateral resolution, was performed on
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43 unsupported Pt_{TD} nanoparticles. The final 3D visualization of top-down synthesized single
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46 nanoparticles confirms the presence of surface concavities, as it is exemplarily illustrated
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49 in Figure 1J (left). Moreover, it is visible that surface concave regions appear on both,
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3 smaller particles, as well as on larger particles. Even though the unsupported
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6 nanoparticles tend to agglomerate, the used tomography technique revealed the irregular
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9 shape of many individual nanoparticles on surface of a bigger nanoparticle cluster, as it
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12 is illustrated in Figure 1J (right side). Compared to the typically spherically shaped
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15 commercial Pt nanoparticles such as the reference catalyst,^{34,35,36} the complex shapes of
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18 Pt_{TD} nanoparticles prefigure an activity increase. However, a representative quantification
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21 of the particularly active sites is not possible due to the individual character of each single
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28 nanoparticle.
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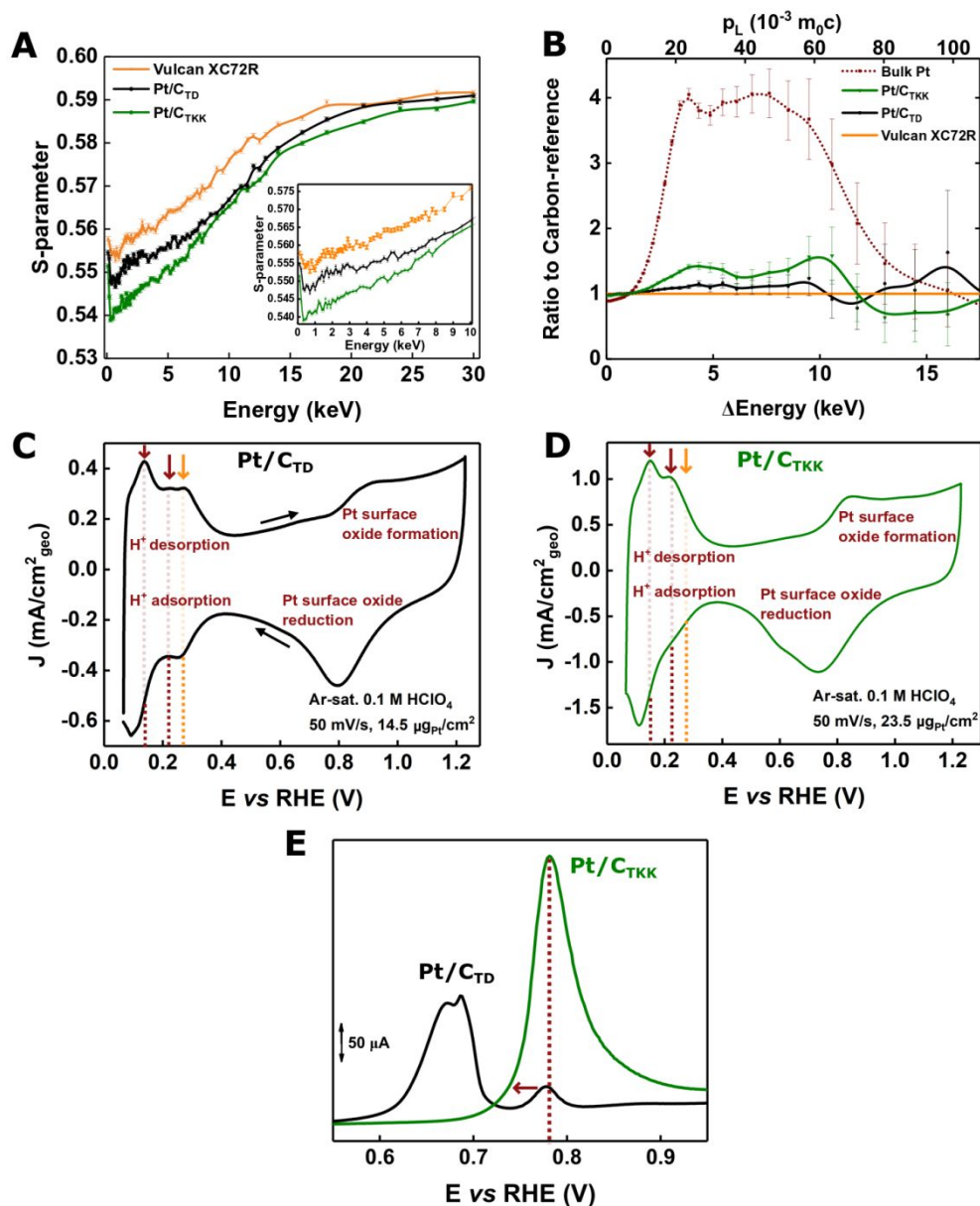


Figure 2. (A) *S*-parameter as a function of the positron implantation energy obtained from DBS measurement. Near the surface, *i.e.*, at low implantation energies, Pt/C_{TD} shows a significantly higher *S*-parameter than commercial Pt/C_{TKK}. The higher *S*-parameter is mainly attributed to the higher defect concentration of Pt/C_{TD}. The inset

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3 shows a magnified energy range of 0-10 keV. (B) Ratio curves normalized to the curve
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6 of the carbon reference obtained by CDBS. Pt/C_{TD} shows a much lower Pt signature
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8 (7.5%) compared to its commercial counterpart (18.2%). Hence, the positron
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10 annihilation probability with Pt core electrons is significantly decreased in Pt/C_{TD}, which
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12 is ascribed to a higher defect concentration. (C,D) Typical CVs of Pt/C_{TD} and
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14 commercial Pt/C_{TKK}, respectively. Electrolyte: Ar-saturated 0.1 M HClO₄. Scan rate: 50
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16 mV/s. Red arrows indicate typical H_{UPD} peak positions of Pt/C_{TKK}. Pt/C_{TD} shows an
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18 additional peak shoulder (orange arrow), which indicates the presence of surface
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20 structural defects (see main text). (E) CO-stripping peaks of Pt/C_{TD} (black curve) and
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22 commercial Pt/C_{TKK} (green curve). The peak shift indicates the presence of surface
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24 structural defects. It has to be noted that the CO-stripping voltammograms were
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26 recorded separately, using a slightly modified setup (see experimental section). CO-
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28 coverage was achieved by bubbling 0.1 M HClO₄ with pure CO for ~6 minutes while
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30 applying a constant potential of 0.1 V *vs* RHE. Saturation of the electrolyte with Ar for
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3 ~30 min, followed by a subsequent performance of a full CV cycle further leads to the
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7 oxidation of the CO monolayer. Scan rate: 20 mV/s.
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14 In order to expand the study of single nanoparticles to the whole system, PAS was
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17 employed. It was chosen to examine the defective character of Pt/C_{TD} in comparison to
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20 commercial Pt/C_{TKK}. PAS is known as a powerful, non-destructive tool to detect open
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23 volume defects, *i.e.*, vacancies or vacancy clusters in a crystal lattice. Due to the effective
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26 trapping of positrons in such crystal defects, the positron is applied as highly-mobile
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29 micro-probe with outstanding sensitivity to vacancy concentrations as low as 10⁻⁷ in
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32 metals.³⁷ For the present study, a low-energy positron beam is required in order to
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35 investigate the near-surface region of the Pt/C samples. For better understanding, some
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38 elementary parts of PAS will be explained in the following text, whereas further details
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42 can be found in the literature.^{38,39} After being implanted in a solid, positrons thermalize
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46 within picoseconds and can then diffuse quasi-freely through the crystal lattice within a
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52 diffusion length typically in the order of 100 nm. They eventually annihilate with a core or
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56 valence electron either in the unperturbed crystal lattice or after being trapped at defect
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3 sites. The positron-electron annihilation leads predominantly to a back-to-back emission
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6 of two 511 keV γ -quanta in the center-of-mass-system. These γ -quanta are most
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9 important for gaining information about defects, as they will be detected during the
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12 experiment. In the laboratory system, the longitudinal component of the electron
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15 momentum (p_L) causes a Doppler-shift of the annihilation quanta. The resulting
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18 broadened annihilation photo peak, *i.e.*, recorded counts as a function of γ -energy, is
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21 analyzed in DBS. For quantitative analysis of the line shape, the so-called S -parameter
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24 is commonly applied, which is defined as the fraction of counts in a fixed central region
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27 around the 511 keV annihilation peak. Since the central part of the annihilation peak is
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30 dominated by positrons annihilating preferably with low-momentum valence electrons, the
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33 S -parameter increases with an increasing number of vacancies or vacancy clusters.⁴⁰ In
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36 CDBS, both γ -quanta of an annihilation event are detected simultaneously in a collinear
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39 detector setup. Due to the effective suppression of the background, the annihilation of
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42 high momentum (core) electrons becomes experimentally accessible, *i.e.*, chemical
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45 information can be gained from the surrounding of the annihilation site. For evaluation,
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48 CDB spectra are normalized, mirrored at 511 keV and usually divided by a reference
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4 spectrum in order to obtain so-called ratio curves in which the elemental signatures can
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7 be clearly observed.
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11 Figure 2A shows the S -parameter as a function of the positron implantation energy, which
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14 is a measure of the probed sample depth.⁴¹ Towards high energies (> 25 keV), the
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17 commercial carbon reference material (Vulcan XC72R) in form of carbon nanoparticles
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20 with a particle size between 30-60 nm,⁴² as well as both the commercial Pt/C_{TKK} and
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23 Pt/C_{TD} nanoparticles supported on Vulcan carbon approach the same S -parameter. This
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26 is expected since at higher energy the positrons are implanted with a higher implantation
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29 depth, *i.e.*, most of the positrons annihilate in the Si substrate. At low energies (< 20 keV),
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32 the carbon reference possesses a higher S -parameter than both the commercial Pt/C_{TKK}
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35 and Pt/C_{TD}. This can be ascribed to the generally lower S -parameter of Pt compared to
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38 the carbon reference, as also observed in the normalized projection of the CDB spectra
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41 (Figure S1) and the low-energy region of the ratio curves (Figure 2B). More interesting,
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46 comparing both samples, Pt/C_{TD} shows a significantly higher S -parameter than
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50 commercial Pt/C_{TKK}. For the interpretation, it has to be mentioned that Pt/C_{TD} and
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3 commercial Pt/C_{TKK} slightly differ in Pt on carbon weight fraction (thermogravimetric
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7 analysis [TGA] reveals ~15 wt.% for Pt/C_{TD} and ~20 wt.% for the commercial Pt/C_{TKK}),
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10 whereas the overall Pt loading on the substrate was adjusted. Therefore, due to its slightly
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13 smaller Pt content a slightly higher *S*-parameter of Pt/C_{TD} compared to commercial
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16 Pt/C_{TKK} was expected. However, the significantly higher *S*-parameter of Pt/C_{TD} cannot be
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19 caused by only the comparably small difference in weight fractions of the samples with
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22 similar overall Pt loading. Instead, this effect is attributed to a higher concentration of
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25 (open-volume) defects in Pt/C_{TD} than in commercial Pt/C_{TKK}. In order to additionally
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28 access the element-specific high-momentum part of the annihilation line related to core
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31 electrons, CDBS was carried out. Figure 2B shows the ratio curves of Pt/C_{TD} and
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34 commercial Pt/C_{TKK} samples. These ratio curves are obtained by normalizing the
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37 individual CDBS raw spectra to same intensity and subsequent division by a reference
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40 spectrum, which is in this case a CDBS spectrum of a carbon reference. For comparison,
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43 a spectrum obtained for a bulk Pt reference is shown as well. For both, Pt/C_{TKK} and Pt/C_{TD},
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46 the typical signature of Pt is visible ($pL=10-80 \times 10^{-3} m_0c$). Assuming a simple model that
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49 positrons annihilate either in defect-free Pt or carbon, one would expect that the
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4 respective Pt signal relates to the measured Pt weight fractions (see TGA result above),
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7 *i.e.*, the Pt signatures in Pt/C_{TD} would amount to 0.75 of that in Pt/C_{TKK}. As determined by
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10 fitting the curves (see SI), however, the Pt signature in Pt/C_{TD} (7.5%) is 0.59 less distinct
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13 than in the commercial Pt/C_{TKK} (18.2%). Hence, the positron annihilation probability with
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16 Pt core electrons is significantly decreased in Pt/C_{TD}. This effect is explained by the
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19 presence of a higher density of vacancy-like defects in Pt/C_{TD}, since positrons are likely
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22 to be trapped at vacancies, where, in turn, the annihilation probability with core electrons
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25 is reduced. This conclusion is in accordance with the lower density of structural defects
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28 in the commercial sample, as observed in the DBS measurements.
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36 Another approach to investigate the presence of structural defects in nanostructured
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39 catalysts is the use of high energy X-rays. Indeed, recent studies have used Rietveld
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42 refinement of WAXS patterns to extract the microstrain (*i.e.*, the local strain) contribution
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45 from the experimental Bragg peak broadening.^{43,44,45} Microstrain broadening in diffraction
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48 data originates in the local atom displacements from their ideal position, such as caused
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53 by atomic vacancies, stacking faults or grain boundaries.⁴⁶ Here, it should be noted that
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3 at the grain boundary of coalescing particles similarly active concave sites are formed.
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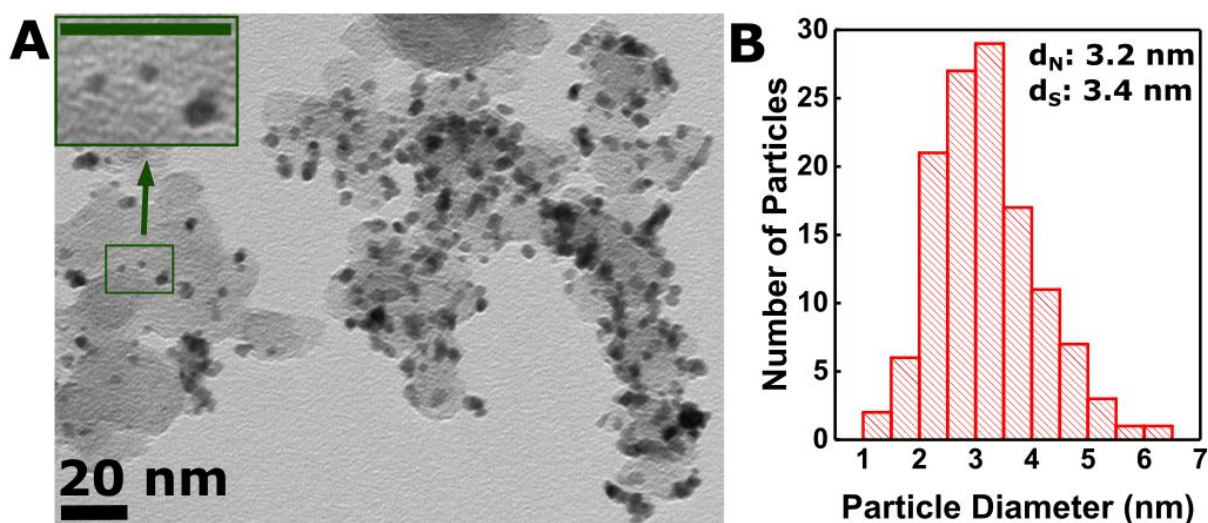
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7 Figure S2A displays the WAXS pattern measured at the ID31 beamline of the European
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10 synchrotron radiation facility (ESRF, Grenoble, France), including the calculated patterns
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13 for the Pt/C_{TD} catalyst (details about the WAXS pattern of the commercial Pt/C_{TKK} catalyst
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16 are available in Figure S2B). Results shown in Table S1 unambiguously support the
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18 conclusions obtained from DBS measurements: while commercial Pt/C_{TKK} features zero
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21 value of microstrain, a value of 0.60% is found for Pt/C_{TD} (being comparable or higher
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24 than some PtNi alloyed samples),⁴⁵ confirming its highly defective structure. The resulting
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27 surface distortion (SD) value was derived as 3.9 ± 0.2 % for the synthesized Pt/C_{TD} (for
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30 further information see reference 45). It has to be noted that both techniques are not
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33 solely surface sensitive, but partially also include bulk information.
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43 Electrochemical measurements further validate the presence of structural surface
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45 defects. Figure 2C and D shows typical cyclic voltammograms (CVs) of Pt/C_{TD} and
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47 commercial Pt/C_{TKK}. In both cases, in the potential range of ~0.05-0.40 V vs the reversible
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50 hydrogen electrode (RHE), typical hydrogen adsorption and desorption ($H_{ads/des}$) features
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3 of polycrystalline Pt are visible. In detail, commercial Pt/C_{TKK} depicts a sharp peak doublet
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6 with maxima at ~0.15 and ~0.22 V *vs* RHE (red dotted lines). According to Vidal-Iglesias
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10 *et al.*, using HClO₄ as an electrolyte, features in the range between 0.09 V and 0.22 V *vs*
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13 RHE can be addressed to the H_{ads/des} on Pt(110) facets, while the impact of (111) and
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16 (100) facets cannot be clearly attributed.⁴⁷ Contrary, Pt/C_{TD} shows an additional distinct
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20 peak shoulder at ~0.27 V *vs* RHE (orange dotted line), which can be assigned to the
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23 H_{ads/des} on defective surface structures, as proposed by Chattot *et al.*⁴⁴ Herein, we assume
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27 that the broad H_{des} peak structure provides further evidence for the presence of structural
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31 defects on the Pt_{TD} nanoparticle surface.
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36 CO-stripping voltammograms of both commercial Pt/C_{TKK} and Pt/C_{TD} are shown in Figure
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39 2E. While the commercial Pt/C only shows a single peak at a potential of ~0.78 V *vs* RHE,
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42 indicating majorly isolated, well-distributed nanoparticles, Pt/C_{TD} shows a peak doublet
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45 with maxima located at ~0.67 V and ~0.69 V *vs* RHE and a singlet at a potential slightly
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48 lower than 0.78 V *vs* RHE. Based on the findings of Maillard *et al.*, appearance of the
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53 peak doublet structure at lower potentials can be traced back to the presence of structural
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3 defects on complex isolated as well as agglomerated nanoparticles.^{44,48} Recently, Chattot
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7 *et al.* compared the ratio between charge Q derived from CO_{ads} and $\text{H}_{\text{ads/des}}$ peaks with
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10 the level of SD of different Pt-based ORR nanocatalysts, indicating a quasi-linear
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13 relationship.⁴⁹ Taken the proposed evaluation protocols into account, $\text{Pt}/\text{C}_{\text{TD}}$ catalyst
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16 shows a $Q_{\text{CO}}/2Q_{\text{H}}$ ratio of 0.85 ± 0.4 , which indicates high density of surface defects and
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21 is comparable to *e.g.*, hollow PtNi/C.
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43 **Figure 3.** (A) TEM image of $\text{Pt}/\text{C}_{\text{TD}}$. The image reveals a homogeneous Pt nanoparticle
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45 coverage of the carbon support, however, parts of the support are less densely covered
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47 than others. The inset shows a magnification of some particles marked by a green
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49 frame (green scale bar: 20 nm). (B) Corresponding PSD of $\text{Pt}/\text{C}_{\text{TD}}$, revealing a number-
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3 averaged diameter (d_N) of $\sim 3.2 \pm 1.0$ nm and a surface-averaged diameter (d_S) of ~ 3.4
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7 nm. The PSD was derived from the investigation of 125 isolated Pt nanoparticles.
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14 Previously mentioned observations can be further validated by observations derived from
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18 TEM imaging, as depicted in Figure 3A. Indeed, several small Pt nanoparticle
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21 agglomerates can be observed. Overall, the Pt nanoparticles are homogeneously
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24 distributed on Vulcan carbon, however, Pt nanoparticle density partially varies. The image
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27 shows that next to particles in the size range of 3-6 nm, several smaller particles with diameter ≤ 2
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30 nm can be observed. The corresponding particle size distribution (PSD) from the
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33 investigation of 125 isolated nanoparticles is given in Figure 3B, taking into account both
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37 edges of each individual particle and no particle agglomerates. PSD analysis was
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41 performed using the ImageJ software. Based on the broad size distribution, the number-
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44 averaged (d_N) and surface-averaged (d_S) diameter of the isolated Pt nanoparticles was
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47 determined to be $\sim 3.2 \pm 1.0$ nm and ~ 3.4 nm, respectively. In case of the commercial
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51 Pt/C_{TKK} sample used, a number-averaged diameter of $\sim 2.8 \pm 0.8$ nm can be found in the
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54 literature.⁵⁰ In contrast to the mean size determined from TEM, WAXS shows a global average
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3 size of 8.3 nm (Table S1), which indicates a bimodal size distribution consisting of smaller,
4 isolated nanoparticles and larger particle aggregates. Similar observations have previously been
5 reported by Chattot *et al.*, where partially aggregated A-Pt/C electrocatalyst showed a TEM
6 derived mean particle size of 3.4 nm, while WAXS revealed a global average size of 7.4 nm.⁴⁵
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13 In order to evaluate the electrocatalytic activity of Pt/C_{TD} towards the ORR, RDE
14 measurements of freshly prepared catalyst inks were conducted. A typical polarization
15 curve of Pt/C_{TD} is depicted in Figure 4A. Evaluation of the kinetic current was performed
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17 using the Koutecký -Levich equation (Equation 1)
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$$I_{kin} = |I \cdot I_{lim}| / |I_{lim} - I| \quad (1)$$

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32 with I being the measured current, I_{kin} being the kinetic current and I_{lim} being the O₂
33 diffusion-limited current of the polarization curve. The kinetic current curve extracted from
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35 the polarization curve in a range of 0.85 V – 1.0 V is shown in the inset of Figure 4A. The
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37 corresponding analysis of commercial Pt/C_{TKK} is depicted in Figure S3. As described
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39 earlier, due to the high concentration of surface structural defects of Pt/C_{TD}, we predict
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41 an activity increase compared to commercial Pt/C. Indeed, at 0.90 V *vs* RHE, we observe
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43 a ~3.6-times enhanced mass activity ($\sim 712 \pm 20$ mA/mg_{Pt}) and a ~6.8-times enhanced
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3 specific activity ($\sim 1.62 \pm 0.32 \text{ mA/cm}^2_{\text{Pt}}$) of Pt/C_{TD} compared to commercial Pt/C_{E-tek}
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7 (activity values taken from literature),^{51,52} and ~ 1.7 -times mass, ~ 2.7 -times specific
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10 activity enhancement compared to Pt/C_{TKK}. The activities of Pt/C_{TKK} are in good
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13 agreement with literature values of the same catalyst, considering the impact of the
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17 ionomer concentration.⁵³ This is a significant improvement over typically used Pt/C
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20 electrocatalysts, especially as the activity is compared to one of the most active
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23 commercial Pt/C catalysts. Moreover, the activity is even comparable to some well-known
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27 PtNi and PtCo alloyed electrocatalysts.^{54,55}

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31 Regarding the stability of Pt/C_{TD}, preliminary accelerated durability tests of Pt/C_{TKK} and Pt/C_{TD}
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33 were conducted in RDE configuration. After 10,000 cycles between 0.6 and 1.0 V vs RHE,
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35 performed at 80°C, Pt/C_{TD} still shows higher activity than Pt/C_{TKK} (Figure S4A). As expected,
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37 post-mortem TEM analysis of Pt/C_{TD} shows strong particle sintering at elevated temperature.
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40 Moreover, isolated particles appear to become more spherical (Figure S4B).
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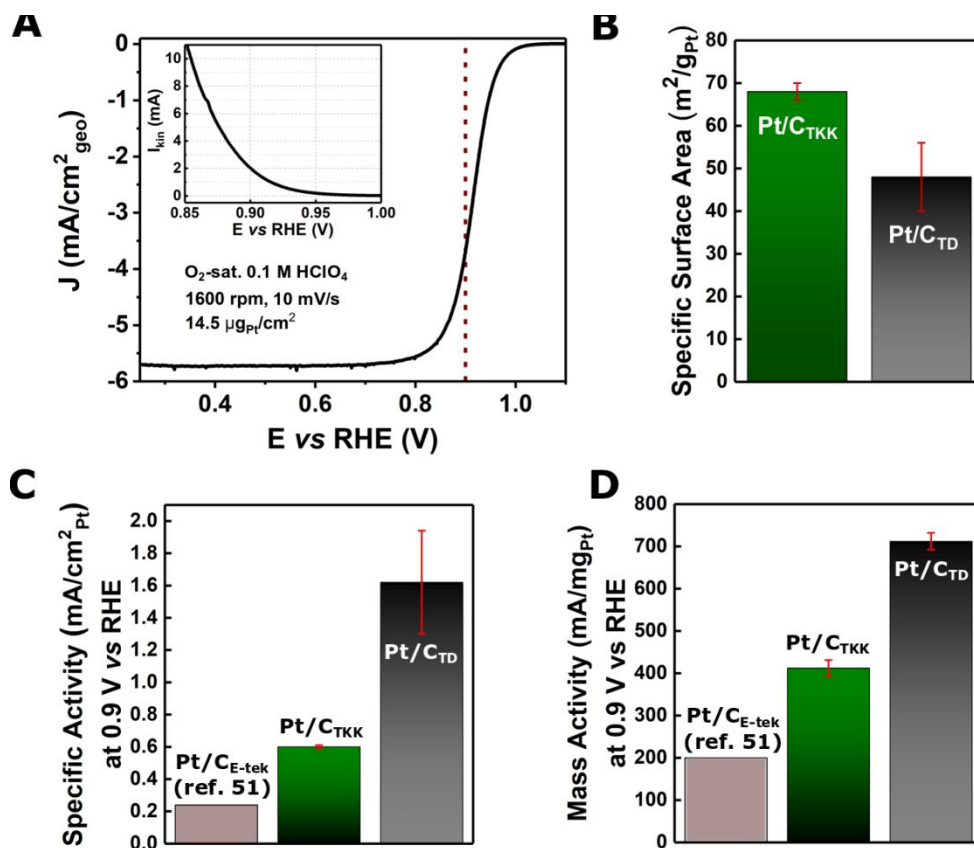


Figure 4. (A) Typical iR -corrected polarization curve of Pt/C_{TD} (anodic scan). Electrolyte: O₂-saturated 0.1 M HClO₄. Scan rate: 10 mV/s. Rotational speed: 1600 rpm. Pseudo-capacitive currents were corrected by subtraction of a background CV. The measurement is normalized to the geometrical area of the glassy carbon electrode used in the experiments (0.196 cm²) and an electrode loading of ~14.5 μg_{Pt}/cm² was adjusted. The corresponding kinetic current curve in a potential range of 0.85 – 1.00 V vs RHE is displayed in the inset of the graph. (B) SSA of Pt/C_{TD} compared to the SSA

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3 of commercial Pt/C_{TKK}. (C) Specific activity of Pt/C_{TD} compared to commercial Pt/C_{E-tek}
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7 (activity value taken from ref. 51, benchmarked under similar conditions) and Pt/C_{TKK} at
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10 0.9 V *vs* RHE. (D) Mass activity of Pt/C_{TD} compared to commercial Pt/C_{E-tek} (activity
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14 value taken from ref. 51, benchmarked under similar conditions) and Pt/C_{TKK} at 0.9 V
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17 *vs* RHE.
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24 To determine the specific activity of Pt/C_{TD}, the kinetic current at 0.90 V *vs* RHE was
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28 normalized to the electrochemically active surface area (ECSA) of the catalyst. Integration
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31 of the H_{UPD} charge of each CV was used to determine the ECSA. For the ad- and
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34 desorption of a monolayer of H on Pt, a charge density of 210 $\mu\text{C}/\text{cm}^2_{\text{Pt}}$ was assumed.
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38 Determination of the mass activity was conducted by normalizing the kinetic current to
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42 the Pt mass deposited on the working electrode.
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45 The specific surface area (SSA) of Pt/C_{TD} was determined to be $\sim 46 \pm 8 \text{ m}^2/\text{g}_{\text{Pt}}$, while
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48 commercial Pt/C_{TKK} exhibits an SSA of $\sim 68 \pm 2 \text{ m}^2/\text{g}_{\text{Pt}}$ (being comparable to literature
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51 data, considering the impact of the ionomer concentration).⁵³ In both cases, the SSA was
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56 normalized to the catalyst mass deposited on the working electrode. Comparing the
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3 average size of both catalysts, only a slightly reduced SSA compared to Pt/C_{TKK} is
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7 expected. Hence, we assume that the actual difference in SSA is partially caused by
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10 agglomeration of the Pt nanoparticles, as can be seen in Figure 3A. The activity data and
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14 SSA values of Pt/C_{TD} and commercial Pt/C are compared in Figure 4B-D.
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18 To further investigate the performance of Pt/C_{TD} in an actual membrane electrode
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21 assembly (MEA), preliminary measurements in a single-cell PEMFC were conducted. To
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25 meet current industrial targets to produce PEMFCs with low Pt content, MEAs with a
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28 cathode loading of $\sim 0.1 \text{ mg}_{\text{Pt}}/\text{cm}^2$ were prepared and examined. The results are shown
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32 in Figure 5. Figure 5A depicts the CO-stripping voltammogram of the Pt/C_{TD} catalyst layer.
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36 As observed in the RDE measurements, the voltammogram shows a characteristic
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39 double peak between 0.6 V and 0.9 V, associated with surface defects. Evaluation of the
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43 SSA gives a value of $\sim 26.5 \text{ m}^2/\text{g}_{\text{Pt}}$, being $\sim 40\%$ lower than the values measured in the
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46 RDE tests (assumed standard charge of a CO monolayer on Pt: $420 \text{ } \mu\text{C}/\text{cm}^2$). This
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50 observation can be due to the increased catalyst batch size, leading to stronger
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54 agglomeration of the Pt nanoparticles, or due to non-uniform ionomer wetting of the
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3 catalyst layer in the MEA. The ORR kinetics of Pt/C_{TD} were extracted from the H₂/O₂
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7 polarization curves after correction of the IR-drop and the H₂ crossover. At 0.9 V, a
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10 noticeable increase of the mass activity compared to Pt/C_{TKK} (Figure 5B, C; reference
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13 data measured in the same setup under identical conditions were taken from literature⁵⁶)
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16 can be observed, validating the results obtained from RDE studies. Owing to the so-called
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19 particle size effect, the specific activity of both catalysts is poorly comparable, as the SSA
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22 of Pt/C_{TKK} is more than 2.5-times larger than the SSA of Pt/C_{TD}.^{56,57} Hence, in order to
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25 compare the intrinsic activity of Pt/C_{TD}, we included the activity data of heat-treated
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28 Pt/C_{TKK} recorded by Schwämmlein *et al.* (HT-Pt/C_{TKK}, taken from literature⁵⁶) with an SSA
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31 of ~7 m²/g_{Pt}. Due to the smaller SSA of HT-Pt/C_{TKK}, higher specific activity is expected.
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34 However, at 0.9 V we still observe higher specific activity of Pt/C_{TD} compared to HT-
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37 Pt/C_{TKK}, indicating higher intrinsic activity of Pt/C_{TD}. While at 0.9 V only kinetic losses are
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40 expected, at higher current densities the low roughness factor (cm²_{Pt}/cm²_{MEA}) leads to a
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43 poor O₂ mass transport, as previously reported by Harzer, Schwämmlein *et al.*^{50,56} Here,
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46 in particular proper wetting of the catalyst layer with ionomer has to be ensured in order
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49 to prevent losses. Thus, we assume that for up-scaled batch sizes, enhancing the SSA
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3 of Pt/C_{TD} through an improved synthesis procedure (*e.g.*, improved mixing of the
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6 electrolyte during synthesis) and adjustment of the ionomer distribution could further
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9 improve the performance of the catalyst, especially at high current densities. Moreover,
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12 in future experimental studies, the stability of defect-rich Pt/C_{TD} in the MEA setup has to
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16 be evaluated, as this task was out of the scope of this work. However, accelerated stress
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19 tests of Schwämmlein *et al.* indicate that in the MEA, a lower SSA has beneficial effects
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22 on the stability of the catalyst, which should be considered prior to adjustment of the
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27 surface area.⁵⁶
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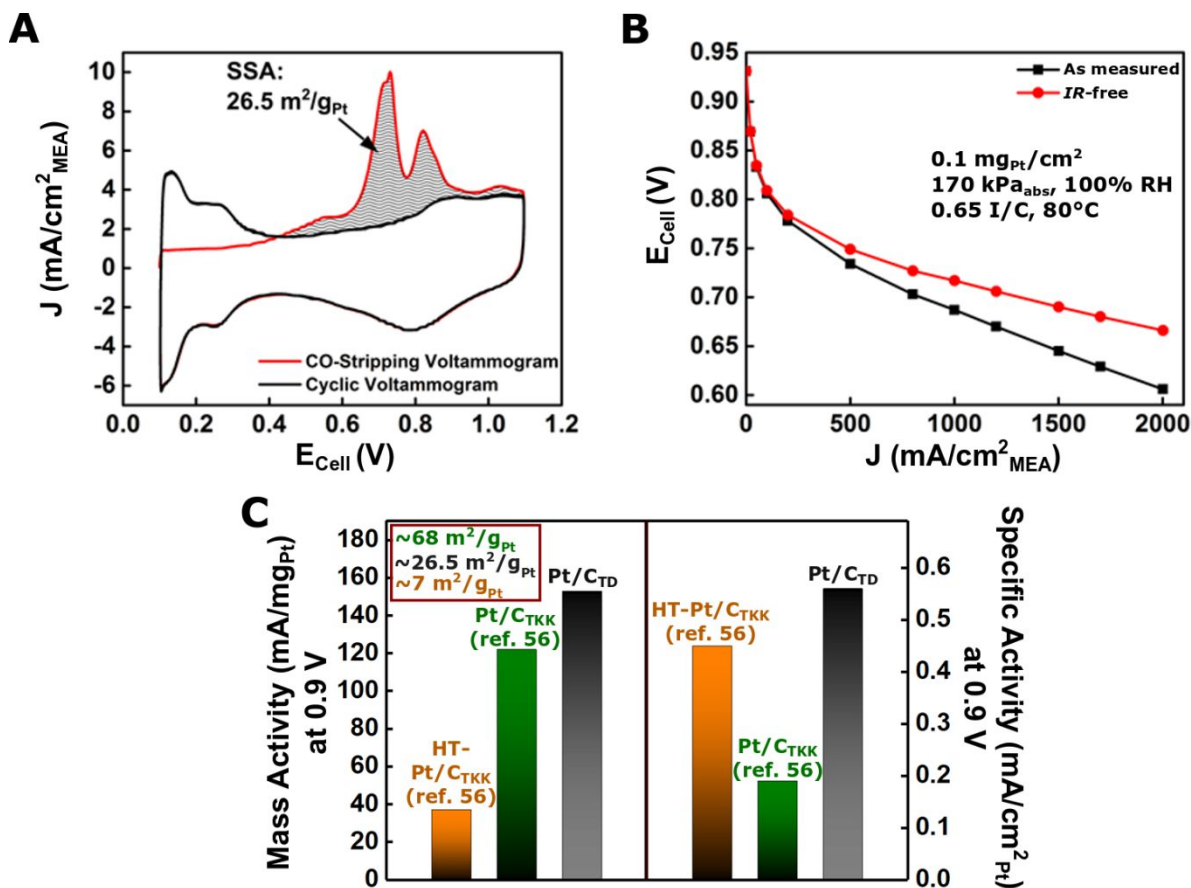


Figure 5. (A) CO-stripping voltammogram of the Pt/C_{TD} cathode catalyst layer, showing a characteristic double peak. Integration of the peaks and normalization to Pt mass leads to a SSA of $\sim 26.5 \text{ m}^2/\text{g}_{\text{Pt}}$. (B) Uncorrected and *IR*-corrected H₂/O₂ differential flow polarization curve of the Pt/C_{TD}-based MEA ($0.1 \text{ mg}_{\text{Pt}}/\text{cm}^2$, 0.65 I/C ratio), recorded at a pressure of $170 \text{ kPa}_{\text{abs}}$, 80°C and 100% relative humidity (RH). (C) Mass and specific activity of Pt/C_{TD} at 0.9 V, compared to Pt/C_{TKK} (SSA: $\sim 68 \text{ m}^2/\text{g}_{\text{Pt}}$) and heat-treated Pt/C_{TKK} (SSA: $\sim 7 \text{ m}^2/\text{g}_{\text{Pt}}$). For activity evaluation, the H₂/O₂ data were corrected for the

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4 *I*_R-drop and the H₂ crossover current. The reference data were taken from reference
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7 56, however, the catalyst was examined in the same setup and under identical
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10 conditions.

16 **Conclusions**

19 Within this work, we show an up-scalable, top-down and one-pot synthetic approach towards
20 highly active Pt/C electrocatalysts, circumventing typical demanding multi-step synthesis
21 procedures. In RDE studies, synthesized Pt/C_{TD} shows high activity towards the ORR with a
22 specific and mass activity of 1.62 mA/cm²_{Pt} and 712 mA/mg_{Pt}, respectively. An ORR activity
23 enhancement over commercial Pt/C was further confirmed in a single-cell PEMFC. Based on
24 TEM, WAXS, CV and PAS experiments, the origin of the superior activity compared to
25 commercial Pt/C can be correlated to the introduction of a high density of surface defects, such as
26 surface concavities. Furthermore, considering the high complexity of classical nucleation driven
27 bottom-up syntheses and costs of the precursor materials, the top-down approach does not only
28 facilitate the synthesis, but should also save overall processing costs in large scale applications.
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46 ASSOCIATED CONTENT

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50 **Supporting Information**
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3 This information is available free of charge on the ACS Publications website. Coincident Doppler
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7 broadening spectrum, WAXS measurements, Rietveld refinement data, Reference ORR
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10 polarization curve, Accelerated durability test, TEM analysis
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17 AUTHOR INFORMATION

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28 **Author Contributions**

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31 The manuscript was written through contributions of all authors. All authors have given
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34 approval to the final version of the manuscript. ‡These authors contributed equally to this
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43 **Notes**

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46 The authors declare no competing financial interest.
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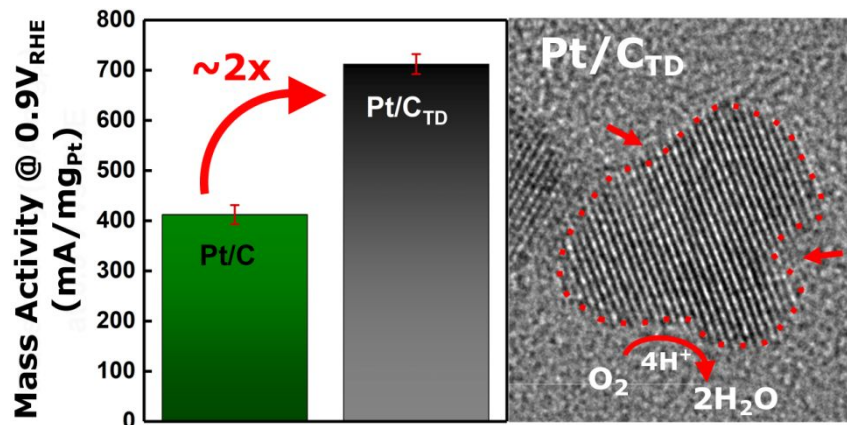
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Tailoring the Oxygen Reduction Activity of Pt Nanoparticles through Surface Defects: A Simple Top-Down Approach



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