

Strong effects of cluster size and air exposure on oxygen reduction and carbon oxidation

electrocatalysis by size-selected Pt_n ($n \leq 11$) on glassy carbon electrodes

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Supporting Information

Electrochemical Setup

The electrochemical setup, especially the UHV part, is described further in Figure S1.

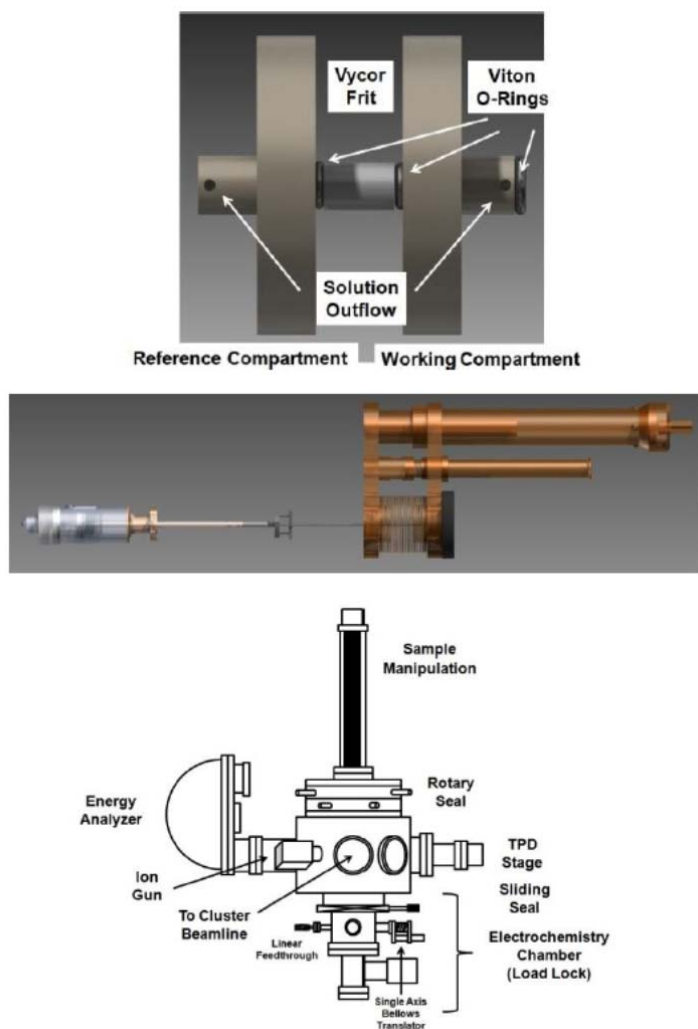


Figure S1. Electrochemical cell for experiments with mass-selected Pt clusters. **Top:** Cell body made out of polyether ether ketone (PEEK). The cell has two compartments, a reference

compartment and a working compartment. The reference compartment contains a Ag/AgCl electrode and aqueous 3M NaCl solution. The working compartment has a Pt wire counter electrode and is pressed with a Viton O-ring against the glassy carbon (GC) working electrode and is filled with 0.1M aqueous HClO₄ solution. The compartments are separated from each other by a Vycor frit (medium coarseness) sandwiched between two Viton O-rings to prevent immediate mixing. Each compartment also includes a Teflon tube for solution inlet and a port for solution outflow. **Middle:** The cell is mounted on a single-axis bellows translator (MDC, left) while the GC electrode (GCE) is mounted on the sample holder and is pressed against the cell via a linear feedthrough (MDC, right). **Bottom:** Schematic of the main chamber of the ion deposition instrument. Cluster deposition on the GCE is carried out in the upper part of the chamber and the electrode is subsequently transferred through the triple sliding seal into the antechamber where the electrochemical measurements are performed. The main chamber contains a hemispherical energy analyzer, an X-ray source, and an ion gun facilitating XPS and ISS measurements.

Preparation of Glassy Carbon Electrodes

Glassy carbon used in the experiments was provided from CH Instruments or ALS Ltd., Tokyo, respectively. The glassy carbon plate P1 (25 mm × 25 mm × 1 mm) was diced into 6 mm × 6 mm × 1 mm squares using a Disco Dad dicing saw. Originally, we attempted to polish these squares with different grades of alumina powder with decreasing particle size (1 μm, 0.3 μm, and 0.05 μm) for at least 20 min in a slurry of the powder and 18 MΩcm water on a polishing microcloth from Buehler. Then the electrodes were sonicated in isopropanol and activated carbon for 20 min,¹ then in 18 MΩcm water, and finally for 20 min in 200 proof ethanol on the sample holder. The electrode was then introduced into the vacuum system via the load lock, backed over night at 400 K, and heated to 900 K for another 60 min in the main chamber (Figure S1). While the polishing procedure was not very successful (it only made

the surface rougher, see Figure S2) it was possible to remove all adventitious oxygen containing species from the glassy carbon electrode via the vacuum heat treatment² (see Figure S3). Because the polished electrodes were rougher than the as-supplied glassy carbon, the electrodes for all measurements described in the paper were simply vacuum heat treated, and were not polished.

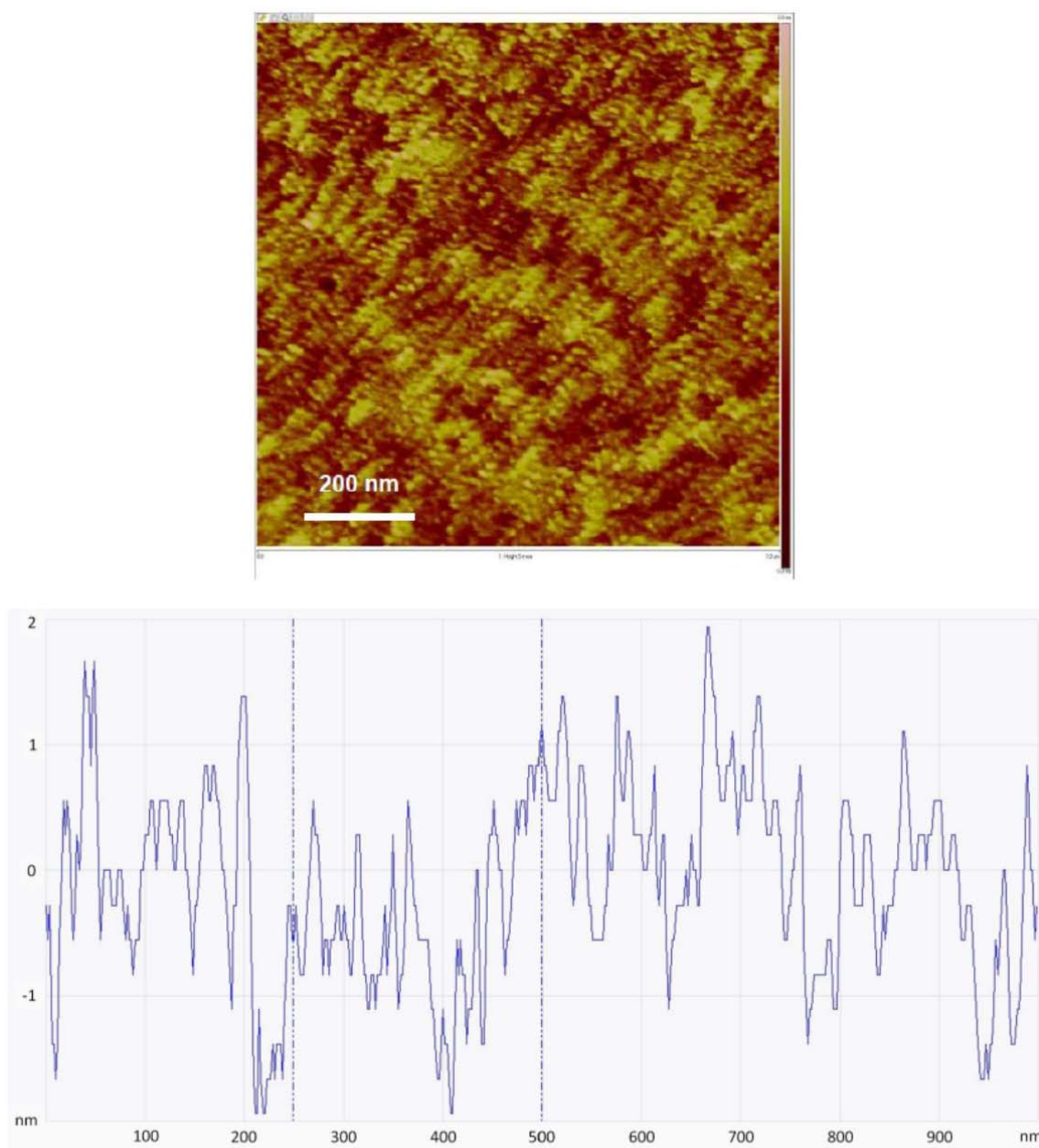


Figure S2 (Part 1). **Top:** AFM image ($1\ \mu\text{m} \times 1\ \mu\text{m}$) and height profile of the as-received glassy carbon electrode material. **Bottom:** Sample height versus the position on the AFM image above.

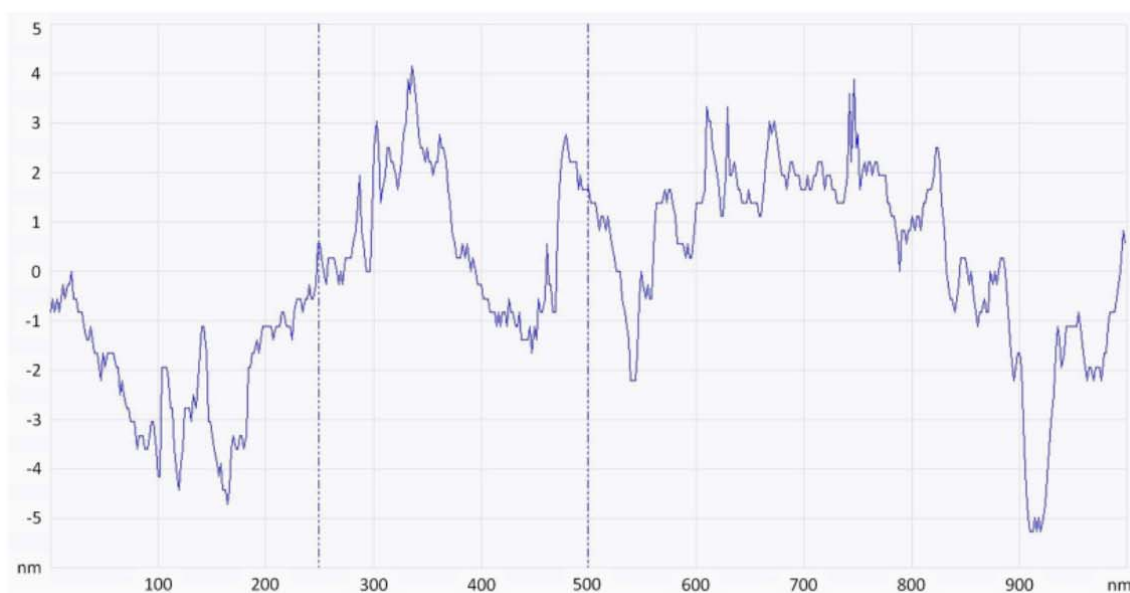
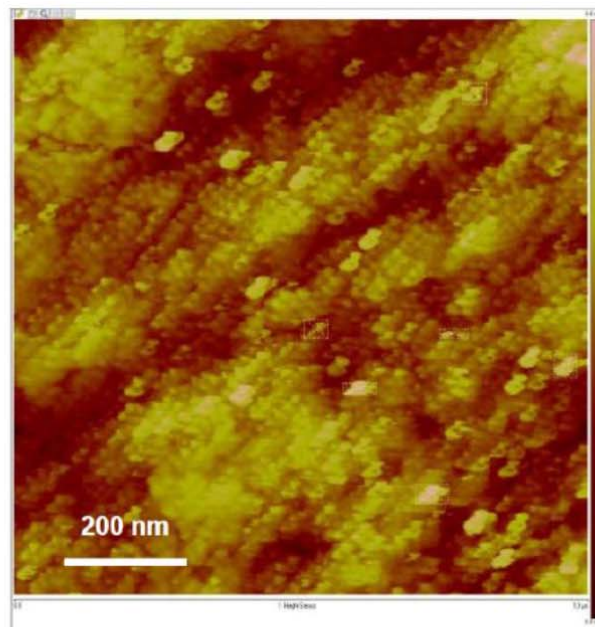


Figure 2 (Part 2). **Top:** AFM image ($1\ \mu\text{m} \times 1\ \mu\text{m}$) and height profile of the polished glassy carbon electrode material. **Bottom:** Sample height versus the position on the AFM image above.

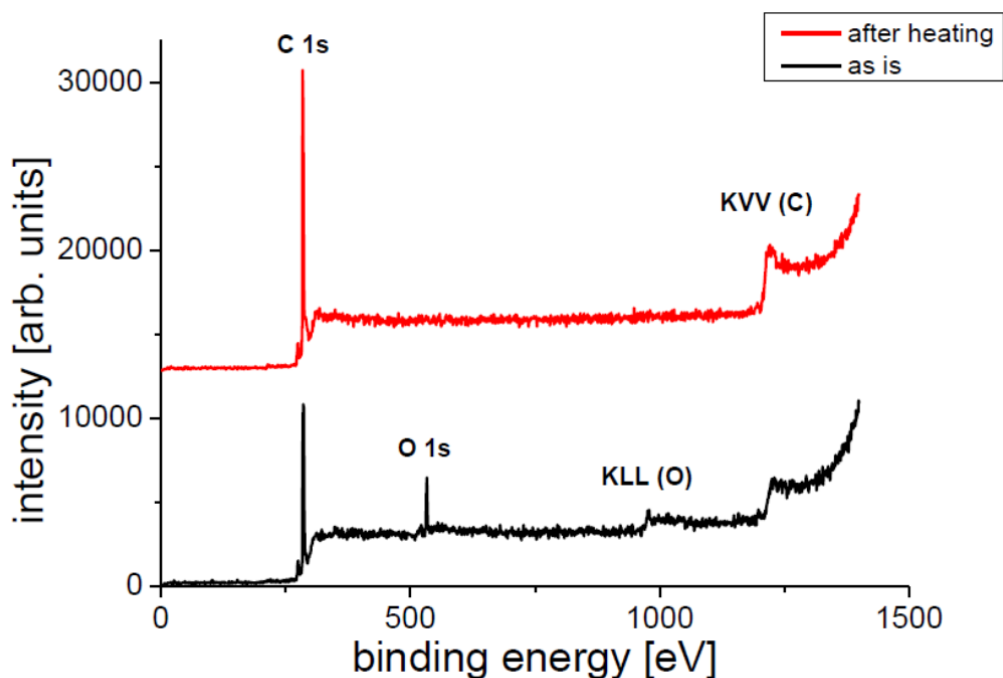


Figure S3. XPS of GCE as received and after heating to 900 K for 60 min under UHV conditions.

Control Experiments

i. Pt_{poly} (Polycrystalline Bulk Platinum) on the benchtop (*ex situ*)

Initial experiments were run on the benchtop in a three-electrode cell constructed in a beaker, using N₂-saturated 0.1M aqueous HClO₄, a Ag/AgCl reference electrode, a Pt wire counter electrode, and a Pt wire working electrode. The Pt wire was cleaned in aqua regia and subsequently electrochemically cleaned via potential cycling between 2 and -2 V vs. Ag/AgCl, at a scan rate of 10 V s⁻¹ for 1000 cycles. A CV between -0.2 V to 1.2 V vs. Ag/AgCl and back was subsequently recorded at a scan speed of 0.05 V s⁻¹, and shows that our results are indeed comparable to results reported in the literature³ (see Figure S4). On the right side of the CV (lower frame of Figure S4), the PtO_x reduction wave can be seen with a maximum at 0.54 V vs. Ag/AgCl (lower trace, initial negative polarity scan) and also a broad plateau from 0.6 to 1.2 V vs. Ag/AgCl representing the oxidation of polycrystalline bulk

platinum wire (upper trace, reverse positive polarity scan). At the left side the H adsorption/desorption features can be observed between 0.1 to -0.2 V vs. Ag/AgCl with bulk hydrogen evolution starting at -0.2 V vs. Ag/AgCl.

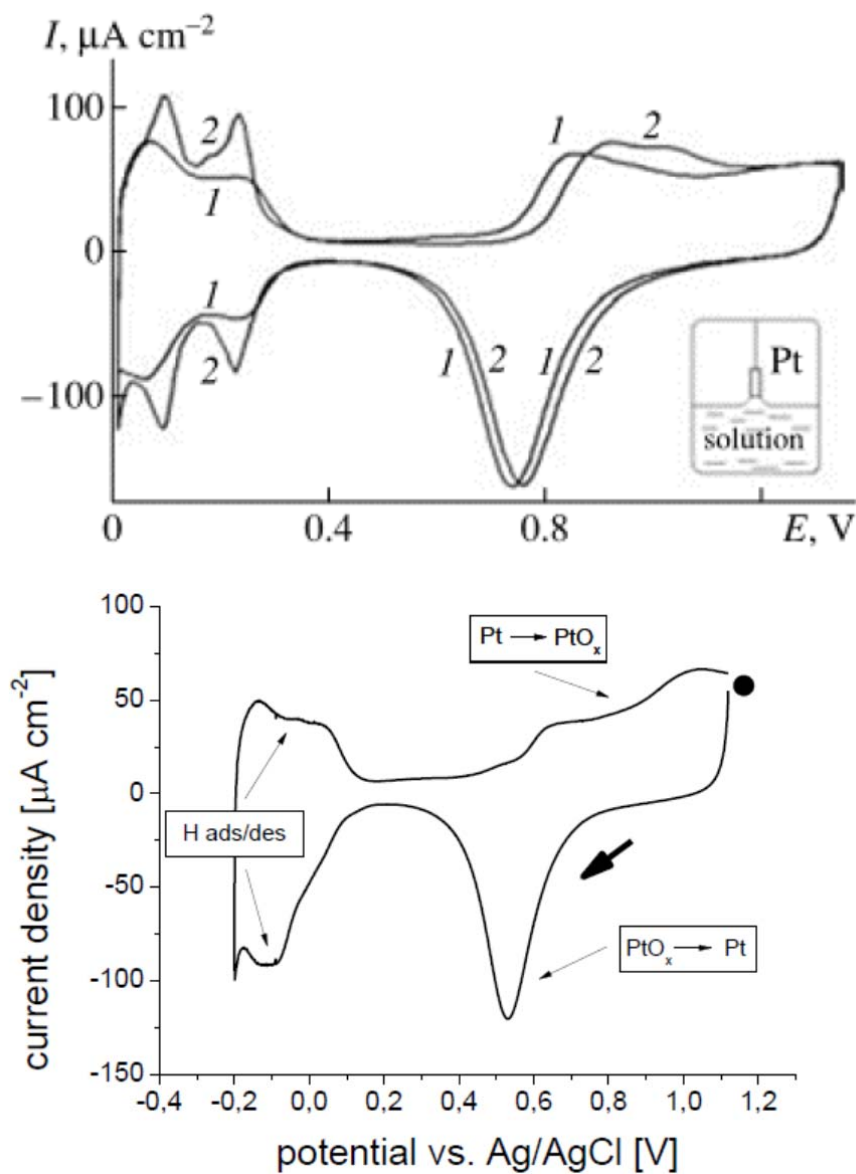


Figure S4. Pt_{poly} *ex situ*. **Top:** Literature results from reference 3 (line 1, potential vs. NHE). Adapted with permission of the Russian Journal of Electrochemistry. **Bottom:** Results obtained in the beaker cell N₂-saturated 0.1M HClO₄, at 0.05 V s⁻¹ beginning at 1.2 V vs. Ag/AgCl).

ii. Pt_{poly} (Polycrystalline Bulk Platinum) in the *in situ* cell

A polycrystalline Pt electrode was fabricated from a scrap of the 99.95% Pt laser vaporization target, and cleaned by immersion in aqua regia, followed by ultrasonication in ethanol. The electrode was mounted to the end of the manipulator in the antechamber and after evacuating the antechamber, the sample was pulled into the UHV end chamber and examined by XPS. The result is shown in the left frame of Figure S5. Note the relatively weak Pt signal and strong signals for O and for C indicating substantial coverage of adventitious adsorbates. The electrode was then sputtered with Ar⁺ for 20 minutes, and subsequently annealed to 1000 K for another 20 minutes, followed by a second XPS examination shown in the middle frame of Figure S5. Note the greatly increased Pt signal, absence of O 1s signal, and near absence of C 1s, indicating that the electrode has an essentially clean metallic Pt surface. The electrode was then inserted into the antechamber, which was pressurized with argon, prior to sealing the Pt_{poly} electrode to the *in situ* electrochemical cell, as described in the Experimental Methods section of the paper. The cell was filled with N₂-saturated 0.1M HClO₄ aqueous electrolyte, and a CV was recorded between 1.3 and -0.1 V vs. Ag/AgCl at a scan rate of 0.1 V s⁻¹. The experiment was then repeated with O₂-saturated 0.1M HClO₄ aqueous solution, and the results are given in the bottom frame of Figure S5. For N₂-saturated electrolyte, the results are comparable to those obtained in the benchtop cell and literature (Figure S4). For O₂-saturated electrolyte, there is additional current in the 0.6 to -0.1 V vs. Ag/AgCl range due to the oxygen reduction reaction (ORR). The current densities obtained with the PEEK cell in the N₂-saturated case are comparable to data obtained from the beaker cell and in the literature. For comparison to experiments with size-selected clusters, the onset of the ORR wave at Pt_{poly} is around 0.8 V vs. Ag/AgCl and a maximum current density of approx. 400 μA cm⁻² is obtained at 0.5 V vs. Ag/AgCl (see bottom frame of Figure S5, red line).

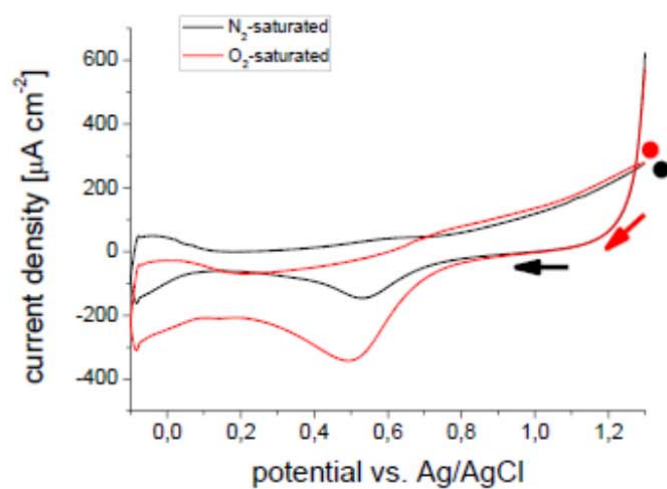
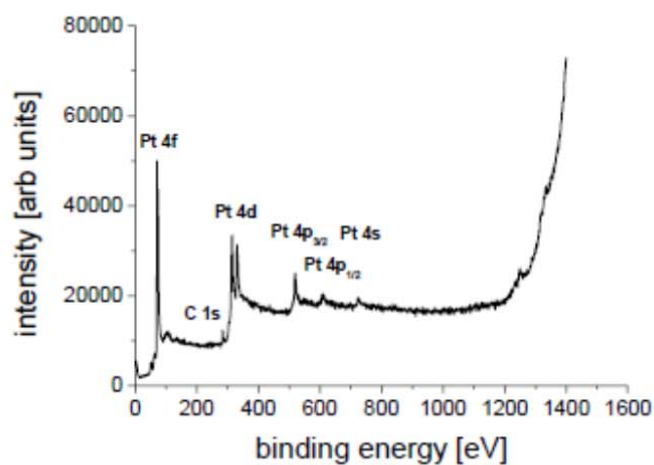
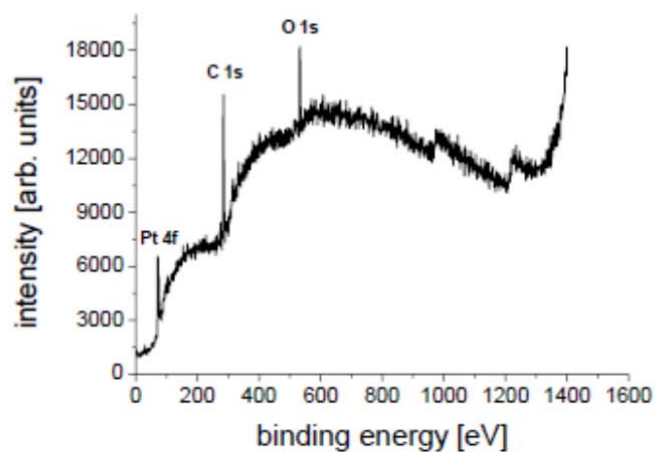


Figure S5. Pt_{poly} *in situ*. **Top:** Polycrystalline Pt electrode after cleaning in aqua regia.

Middle: Polycrystalline Pt electrode after sputtering and annealing. **Bottom:** Polycrystalline platinum electrode in PEEK cell under N_2 - and O_2 -saturated conditions in 0.1M HClO_4 at a

scan rate of 0.1 V s^{-1} beginning at 1.3 V vs. Ag/AgCl . Voltammetry curves have been smoothed using the Savitzky-Golay method.

iii. Pure glassy carbon electrodes (*in situ*)

A glassy carbon electrode was treated as described above and subjected to electrochemical experiments in N_2 - and O_2 -saturated 0.1M HClO_4 (see Results section in main paper). Figure S6 shows an optical microscopy image of the electrode after being removed from the electrochemistry chamber.

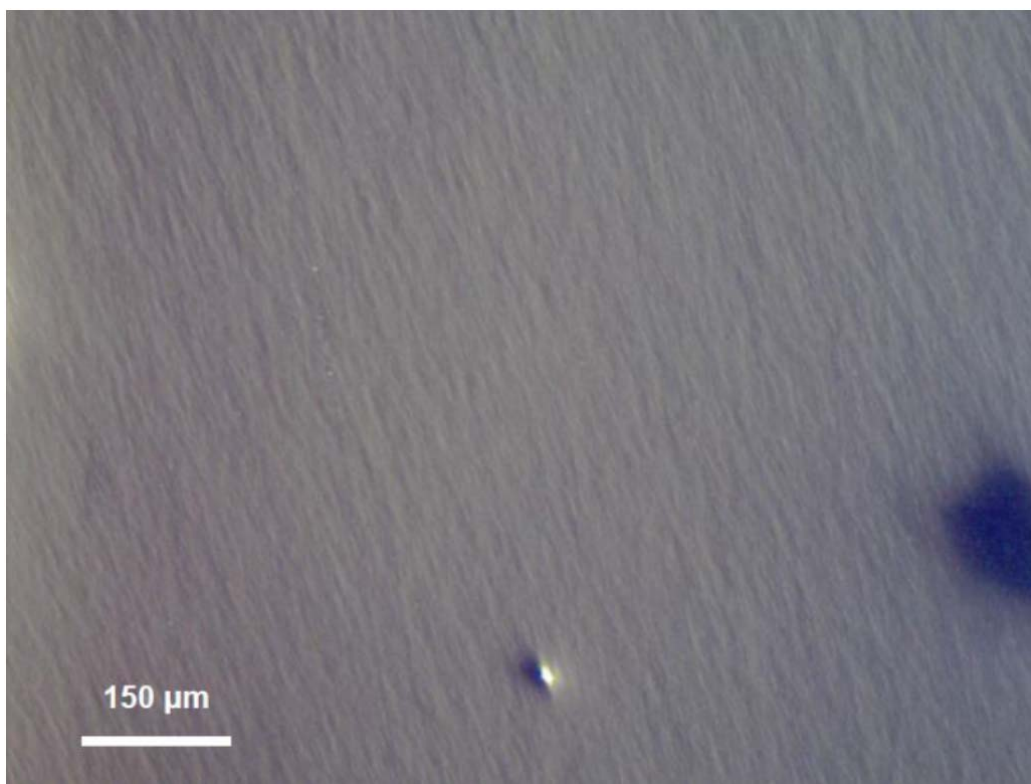


Figure S6. Optical microscope image of the GC electrode after *in situ* electrochemical experiments.

iv. GCE with solution-deposited Pt (Pt_{nano})

Conventional Pt particles on a GCE were prepared via the procedure described in the Experimental section of the main paper. Figure S7 depicts the XPS and SEM results obtained

on these particles of 1 ML Pt deposited on glassy carbon. The middle frame of Figure S7 shows a shift of the Pt 4f peaks towards lower binding energies upon reduction of the hexachloroplatinic acid, namely the Pt 4f_{7/2} peaks has a binding energy of 71.2 eV corresponding to that of bulk platinum.

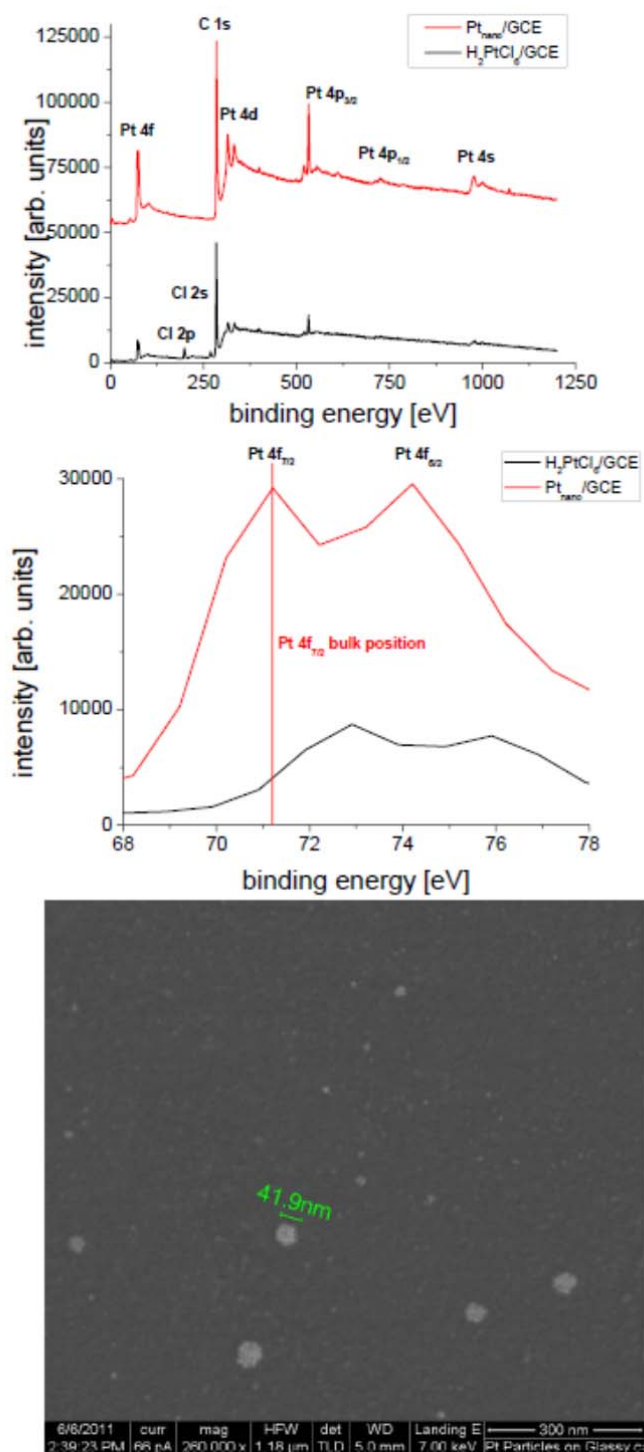


Figure S7. H₂PtCl₆/GCE and Pt_{nano}/GCE (1 ML Pt). **Top:** XPS survey scan. **Middle:** Region scan of the Pt 4f peak. The Pt 4f_{7/2} peak is at 71.2 eV for the bulk metal which coincides with the peak for Pt_{nano}/GCE (straight red line). **Bottom:** SEM image of Pt_{nano}/GCE.

In Situ Experiments on Size-Selected Pt_n/GCE

Initial investigations included XPS and ISS measurements on Pt_n/GCE after *in situ* electrochemical experiments. A similar amount of Pt₁ (10% of a ML) was deposited on both glassy carbon (as described above) and rutile TiO₂(110). The TiO₂ was sonicated in ethanol already mounted to the sample holder for 20 min, introduced into the load lock which was pumped down to 5×10^{-8} Torr (approx. 2 h), transferred to the main chamber, sputtered with Ar⁺ for 20 min, and finally annealed for another 20 min prior to deposition. The Pt 4f_{7/2} peak positions of the respective clusters have been determined by using a Gauss-Lorentz fit, GL(30), within CasaXPS (Figure S8). The fits were carried out with a fixed Pt 4f_{7/2} and 4f_{5/2} peak separation of the literature value of 3.33 eV and variable peak widths. Each cluster size, except Pt₁₁ has been carried out at least twice. The error bars in Figure 4 in the main paper arise from the standard deviation from the different observed peak positions (fits), except for Pt₁₁, here it arises from changing the peak position in the fit until it becomes unreasonable (the uncertainty is in the range of $\sim \pm 0.1$ to 0.2 eV). Figure S9 shows the comparison of the XPS and ISS results of Pt₁/TiO₂ and Pt₁/GCE (further discussion is presented in the Results section of the main paper).

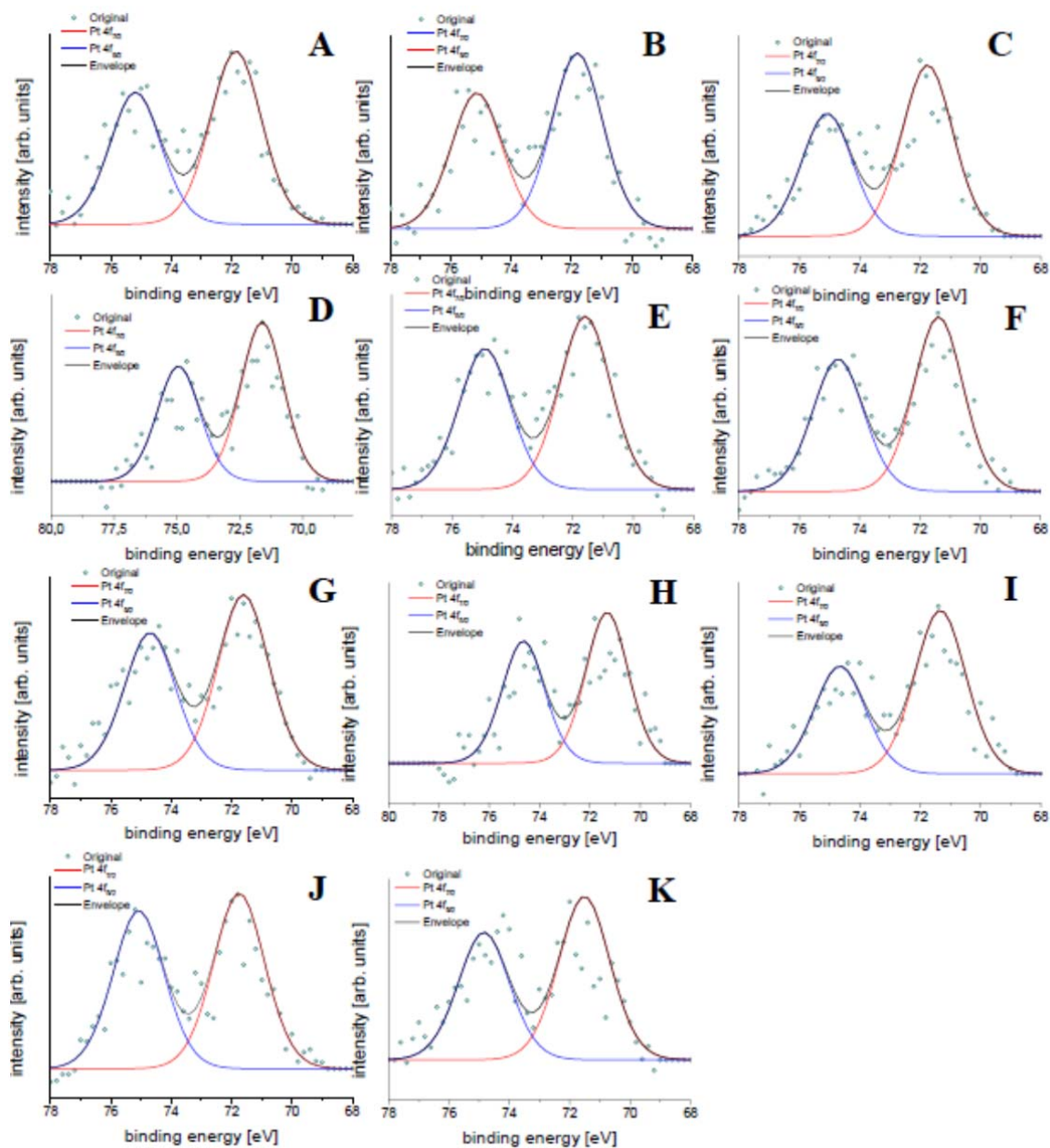


Figure S8. XPS region scans of the Pt 4f peaks of Pt_n/GCE (n = 1 – 11, A - K) as-deposited.

XPS spectra were fit using a Gauss-Lorentzian procedure.

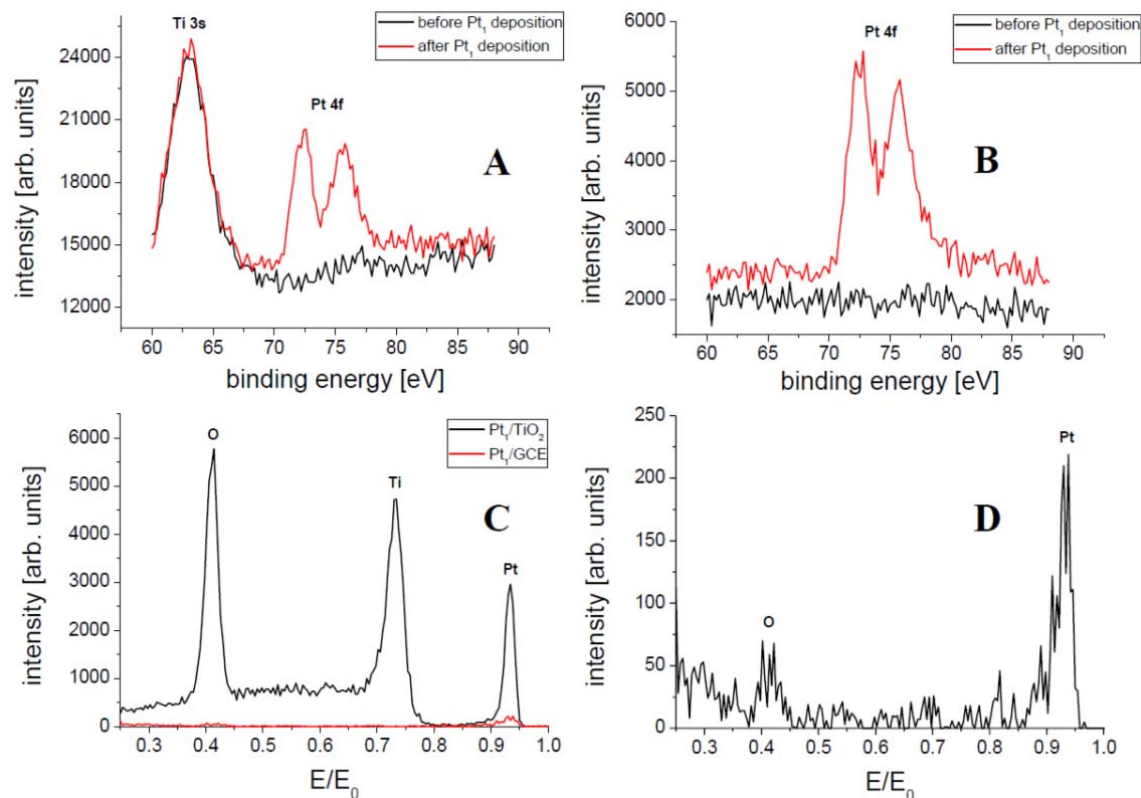


Figure S9. XPS and ISS of Pt₁. **A:** Pt 4f XPS signal of Pt₁/TiO₂. **B:** Pt 4f XPS signal of Pt₁/GCE. **C:** ISS trace of Pt₁/TiO₂ (black) compared to Pt₁/GCE (red). **D:** ISS trace of Pt₁/GCE.

ii. Electrochemistry of Pt_n on GCEs (*in situ*)

Electrochemical experiments of Pt₁, Pt₂, Pt₃, Pt₅, Pt₆, and Pt₈/GCE are presented below in Figure S10 to Figure S16. Experiments were performed in a 0.1M HClO₄ aqueous electrolyte. In order to evaluate the role of the perchlorate ion in the carbon oxidation reactions (see main paper), Pt₉/GCE was additionally investigated in a 0.1M H₂SO₄ aqueous electrolyte (Figure S17).

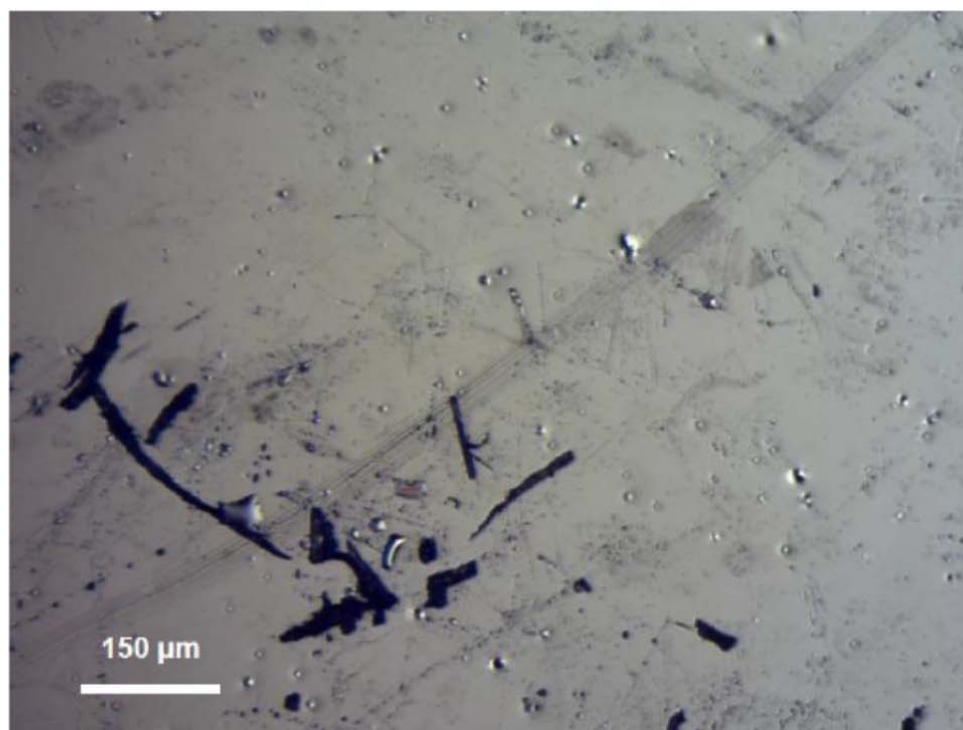
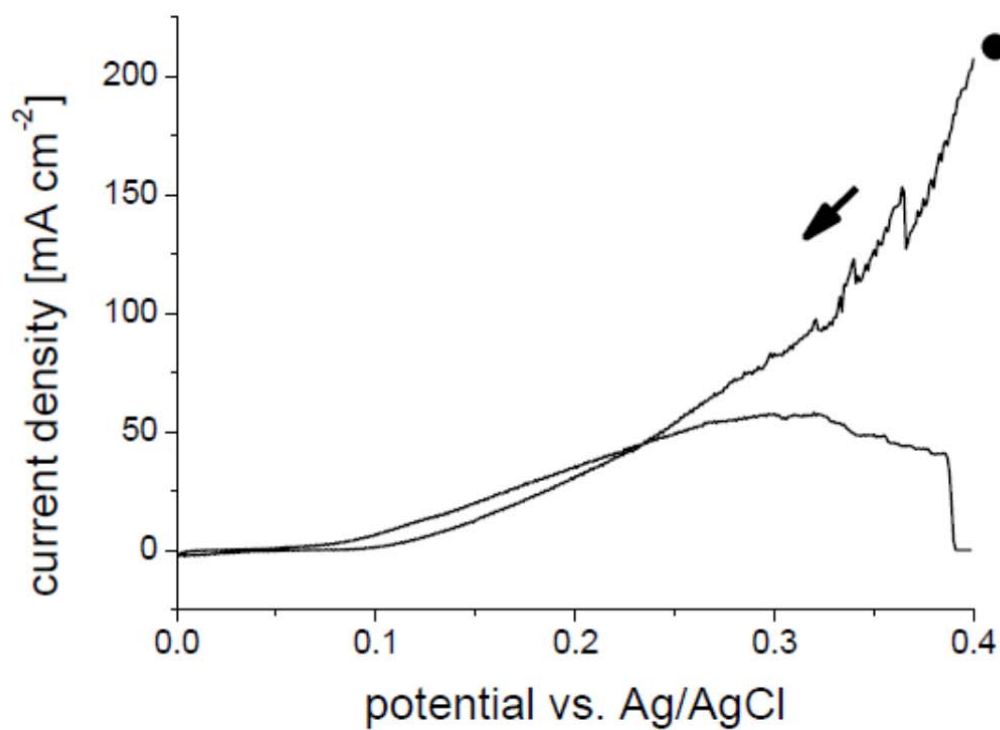


Figure S10. Pt₁/GCE *in situ* (0.1 ML Pt). **Top:** CV of Pt₁/GCE in N₂-saturated 0.1M HClO₄ at a scan rate of 0.1 V s⁻¹ beginning at 0.4 V vs. Ag/AgCl. **Bottom:** Optical microscope image of the Pt₁/GC electrode after the electrochemical measurements.

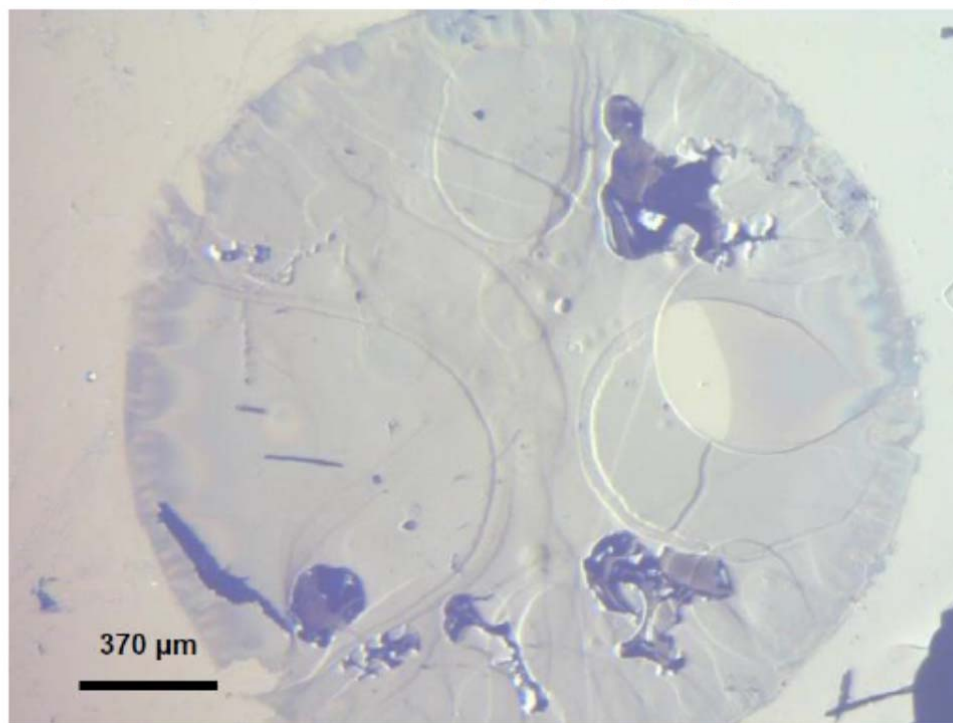
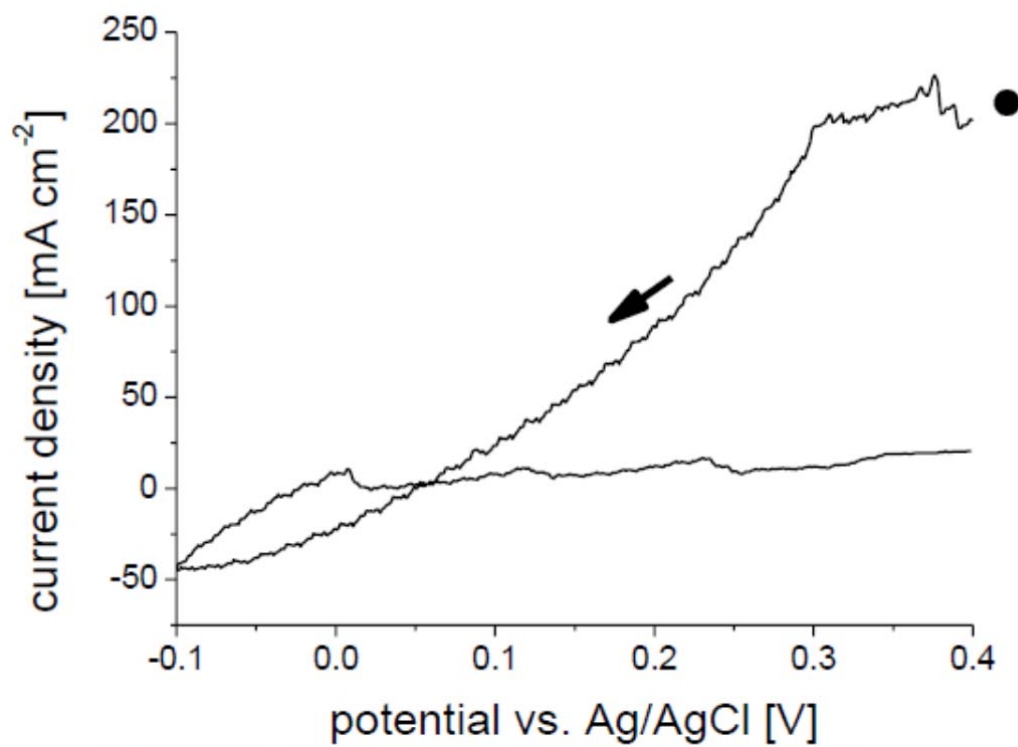


Figure S11. Pt_2/GCE *in situ* (0.1 ML Pt). **Top:** CV of Pt_2/GCE in N_2 -saturated 0.1M HClO_4 at a scan rate of 1 V s^{-1} beginning at 0.4 V vs. Ag/AgCl. **Bottom:** Optical micrograph of the Pt_2/GC electrode after the electrochemical measurements.

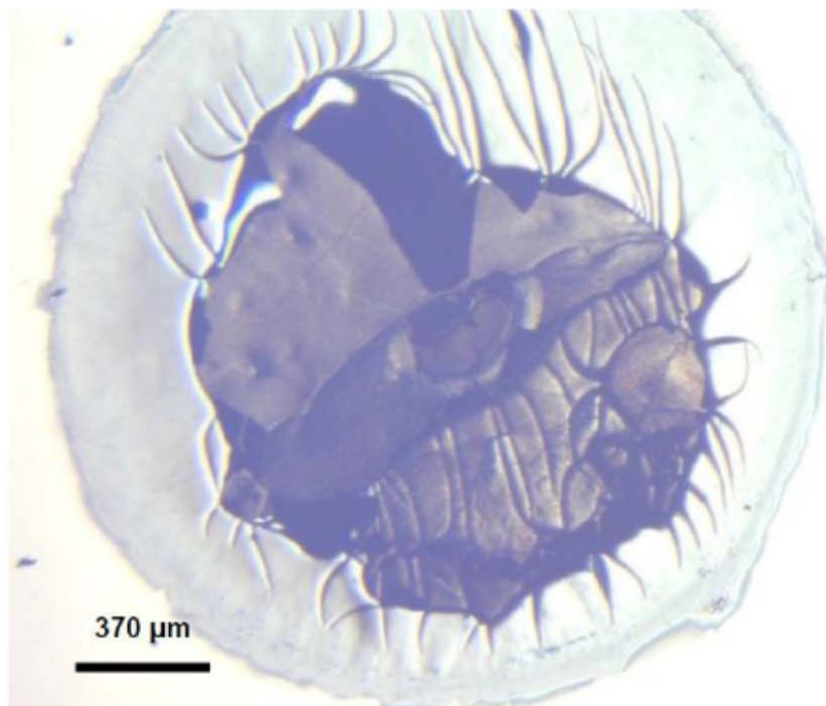
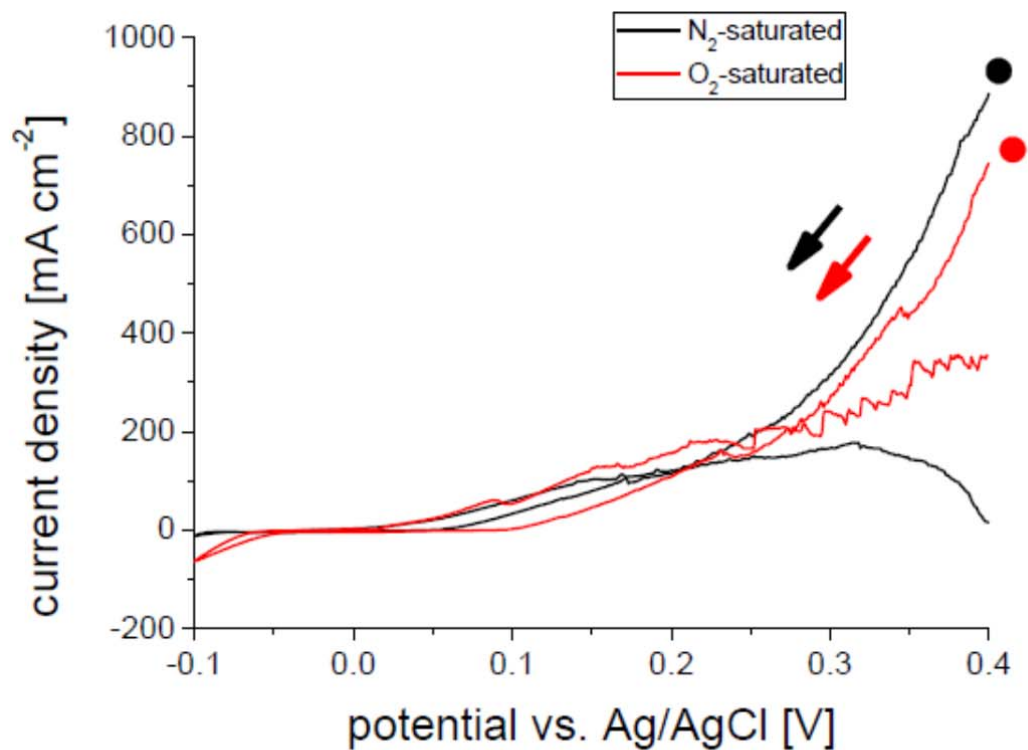


Figure S12. Pt₃/GCE *in situ* (0.1 ML Pt). **Top:** CV of Pt₃/GCE in N₂- and O₂-saturated 0.1M HClO₄ at a scan rate of 0.1 V s⁻¹ beginning at 0.4 V vs. Ag/AgCl. **Bottom:** Optical micrograph of the Pt₃/GC electrode after the electrochemical measurements.

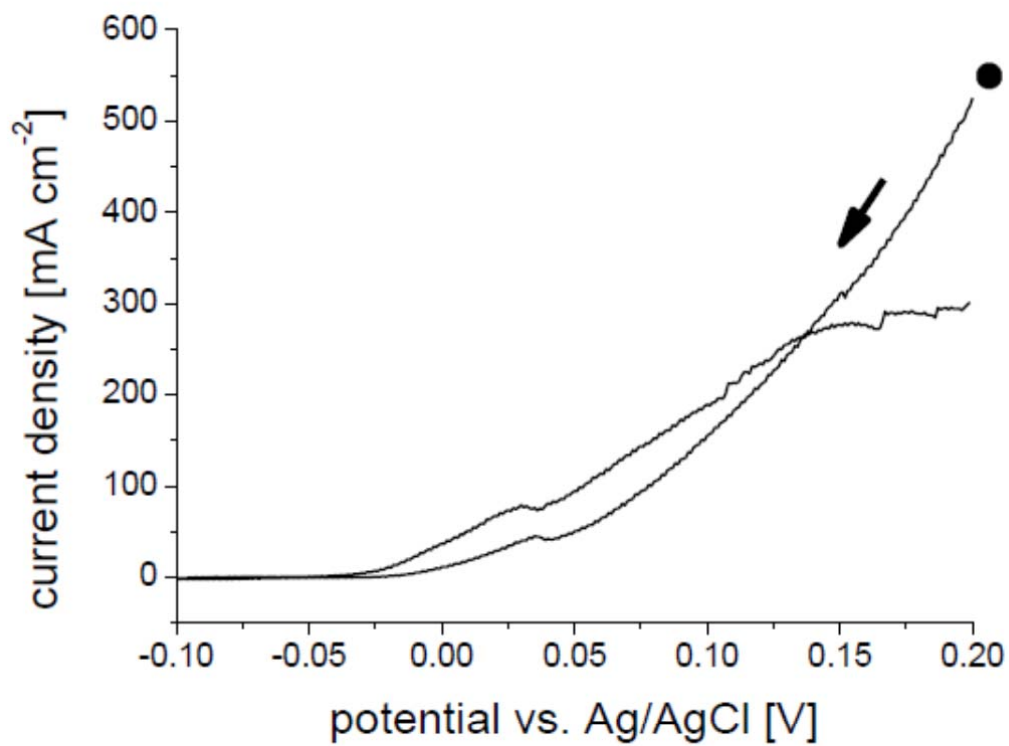


Figure S13. Pt_5/GCE *in situ* (0.1 ML Pt). **Top:** CV of Pt_5/GCE in N_2 -saturated 0.1M HClO_4 at a scan rate of 0.1 V s^{-1} beginning at 0.2 V vs. Ag/AgCl. **Bottom:** Optical micrograph of the Pt_5/GC electrode after the electrochemical measurements.

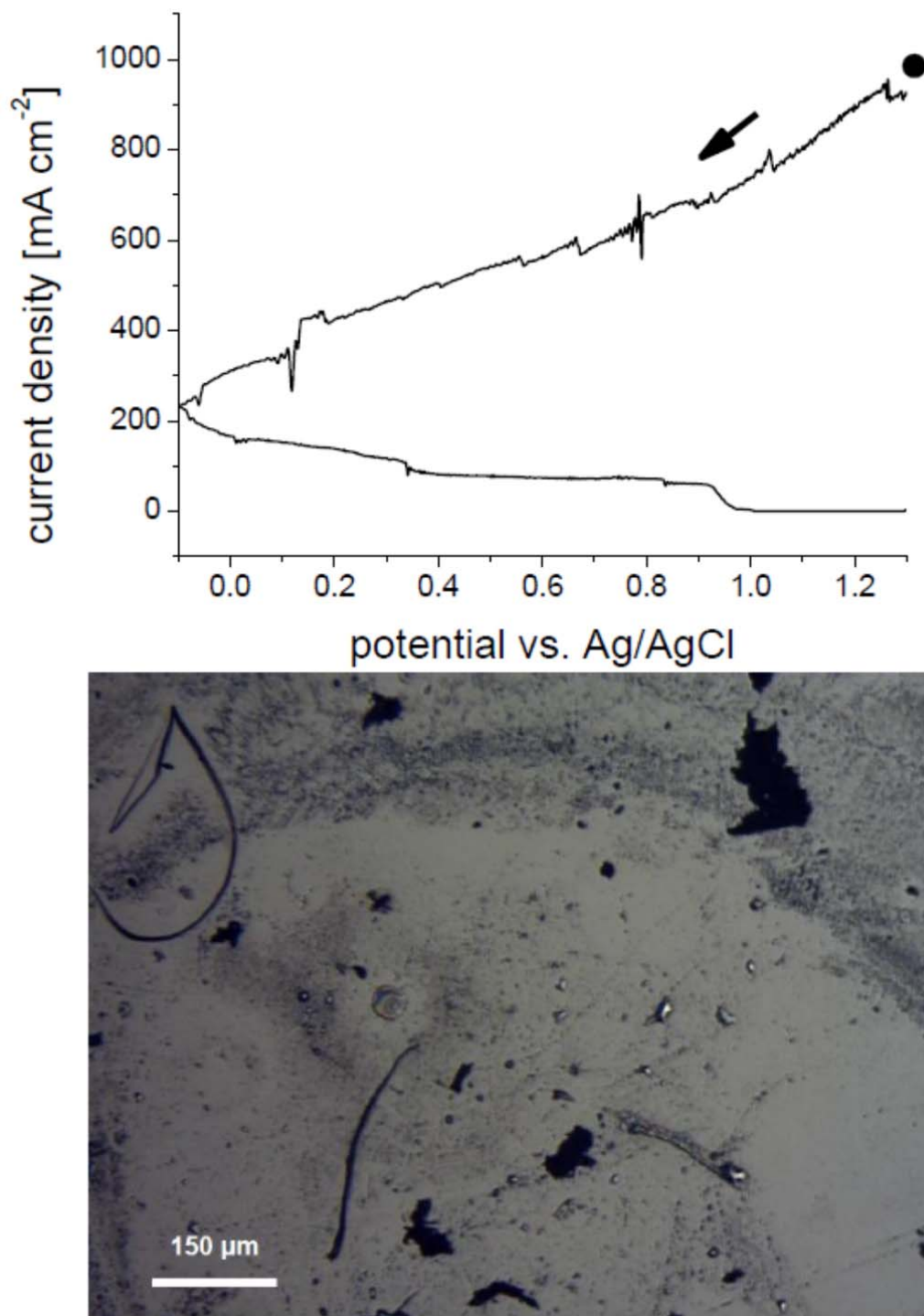


Figure S14. Pt₆/GCE *in situ* (0.1 ML Pt). **Top:** CV of Pt₆/GCE in N₂-saturated 0.1M HClO₄ at a scan rate of 1 V s⁻¹ beginning at 1.3 V vs. Ag/AgCl. **Bottom:** Optical micrograph of the Pt₆/GC electrode after the electrochemical measurements.

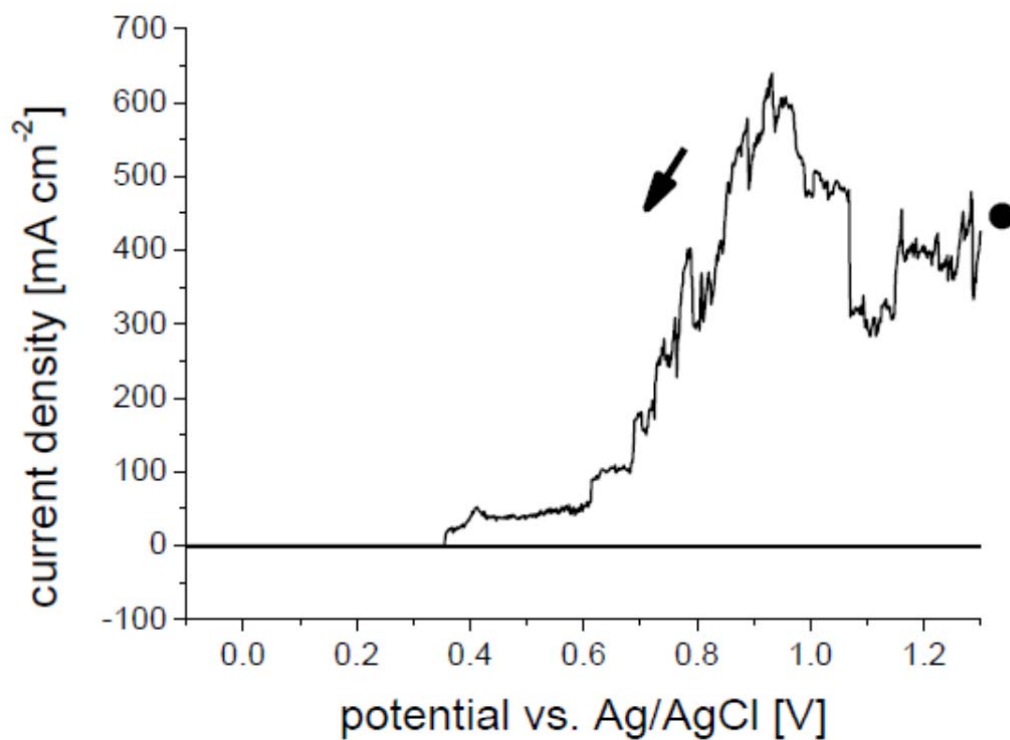


Figure S15. Pt₈/GCE *in situ* (0.1 ML Pt). **Top:** CV of Pt₈/GCE in O₂-saturated 0.1M HClO₄ at a scan rate of 0.1 V s⁻¹ beginning at 1.3 V vs. Ag/AgCl. The current dropped to zero on the initial scan due to gas evolution. **Bottom:** Optical micrograph of the Pt₈/GC electrode after the electrochemical measurements.

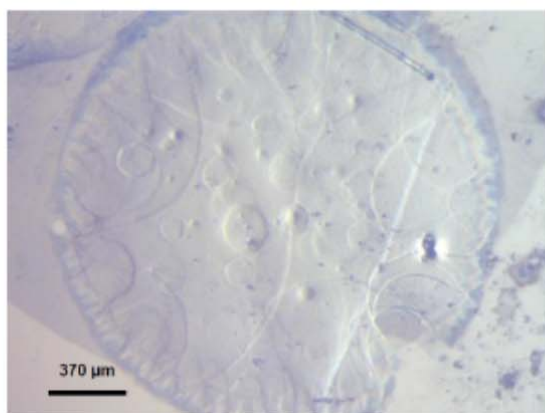
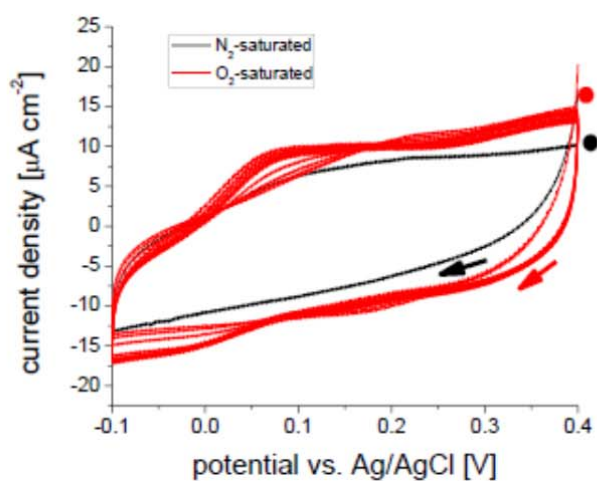
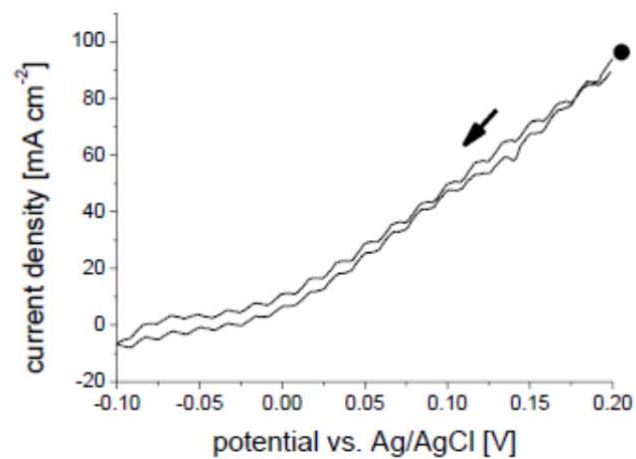


Figure S16. Pt₁₀/GCE *in situ* (0.1 ML Pt). **Top:** CV of Pt₁₀/GCE in N₂-saturated 0.1M HClO₄ at a scan rate of 1 V s⁻¹ (initial scan from 0.2 to -0.1 V vs. Ag/AgCl). **Middle:** CVs of Pt₁₀/GCE in N₂- and O₂-saturated 0.1M HClO₄ at a scan rate of 0.1 V s⁻¹ (initial scan from 0.4

to -0.1 V vs. Ag/AgCl), 10 scans in the O₂ case. **Bottom:** Optical micrograph of the Pt₁₀/GC electrode after the electrochemical measurements.

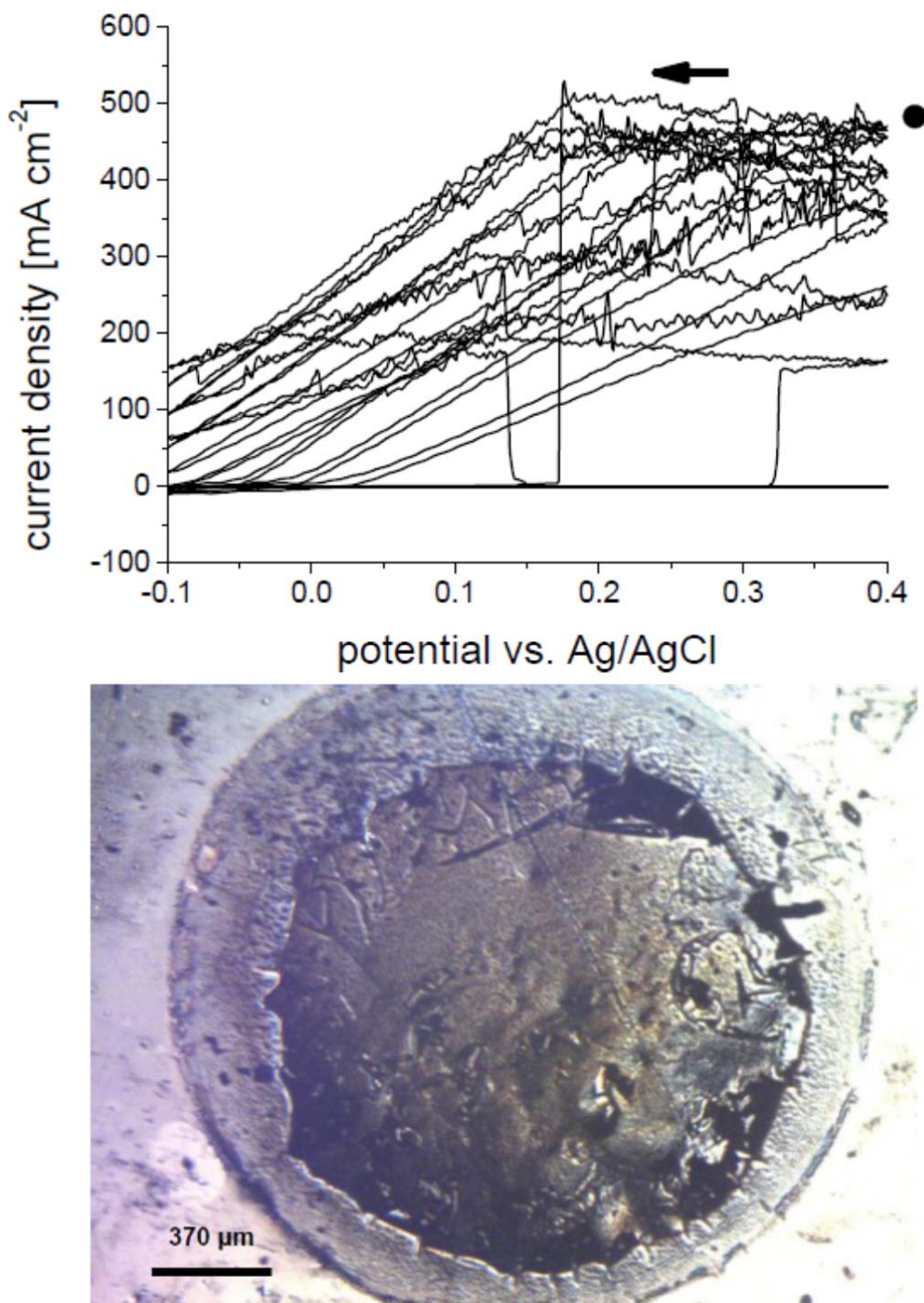


Figure S17. Pt₉/GCE *in situ* (0.1 ML Pt). **Top:** CV (100 scans) of Pt₉/GCE in N₂-saturated 0.1M H₂SO₄ at a scan rate of 1 V s⁻¹ beginning at 0.4 to -0.1 V vs. Ag/AgCl. The current

dropped to zero on the initial scan due to gas evolution on the 10th scan. **Bottom:** Optical microscope image of the Pt₉/GC electrode after the electrochemical measurements in 0.1M H₂SO₄.

Ex Situ Experiments on Size-Selected Pt_n/GCE

The *ex situ* experiments on Pt_n clusters deposited on GC are described in the Experimental section of the main paper. Also the results on Pt₇/GCE (Figure 9), Pt₄/GCE (Figure 10), and Pt₉/GCE (Figure 11) are presented there. Additionally, shown here are the results for Pt₃/GCE (Figure S18), Pt₅/GCE (Figure S19), and Pt₆/GCE (Figure S20). While the CVs for Pt₃/GCE are similar to the ones for Pt₄/GCE (a very active carbon oxidation catalyst), the results for Pt₅/GCE and Pt₆/GCE gradually approach the behavior of Pt₇/GCE (not active for carbon oxidation). Both show stable CV curves of the redox activity of an adsorbate from the air. This can especially be observed for Pt₆/GCE (middle frame of Figure S20), however after 250 cycles the adsorbate seems to be gone and the CV in O₂-saturated solution becomes more or less featureless (top frame of Figure S20, red line).

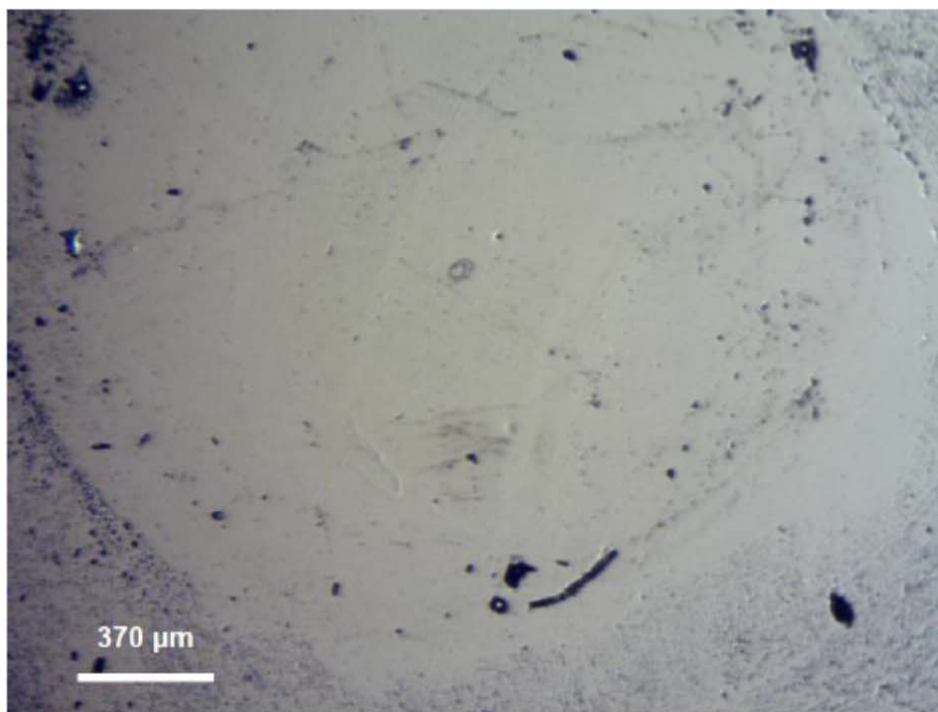
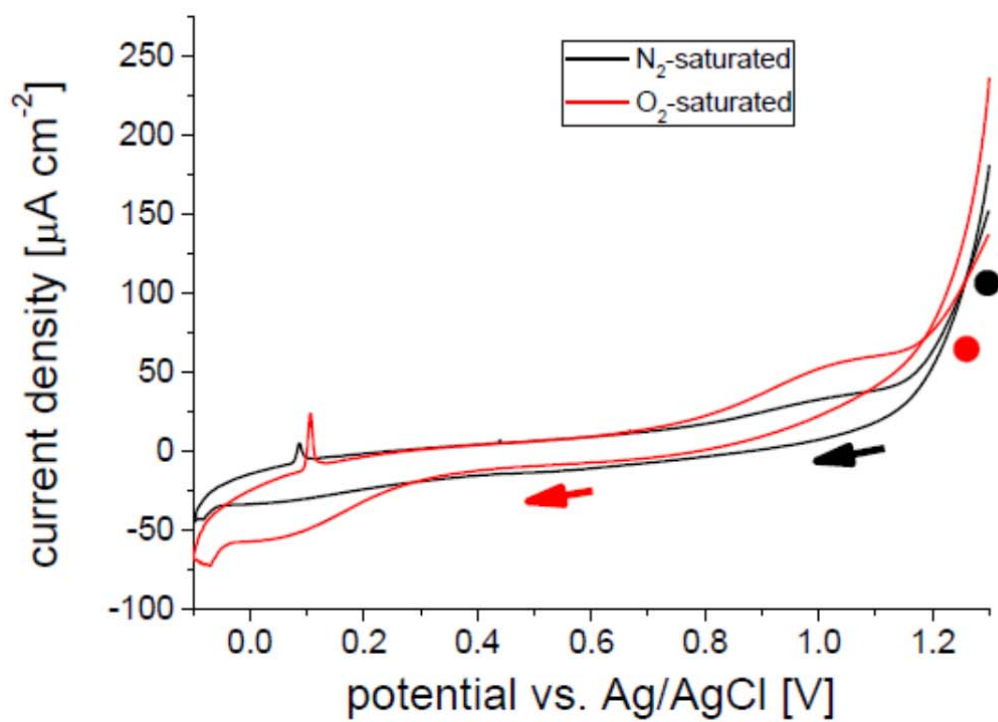


Figure S18. Pt₃/GCE *ex situ* (0.1 ML Pt). **Top:** CV of Pt₃/GCE in N₂- and O₂-saturated 0.1M HClO₄ at a scan rate of 0.1 V s⁻¹ beginning at 1.3 V vs. Ag/AgCl. **Bottom:** Optical microscope image of the Pt₃/GC electrode after the electrochemical measurements.

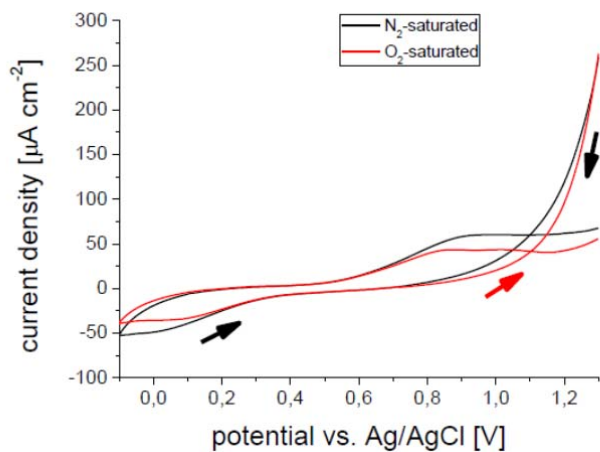


Figure S19. Pt₅/GCE *ex situ* (0.1 ML Pt). CV of Pt₅/GCE in N₂- and O₂-saturated 0.1M HClO₄ at a scan rate of 0.1 V s⁻¹ beginning at 1.3 V vs. Ag/AgCl. (No electrode image available.)

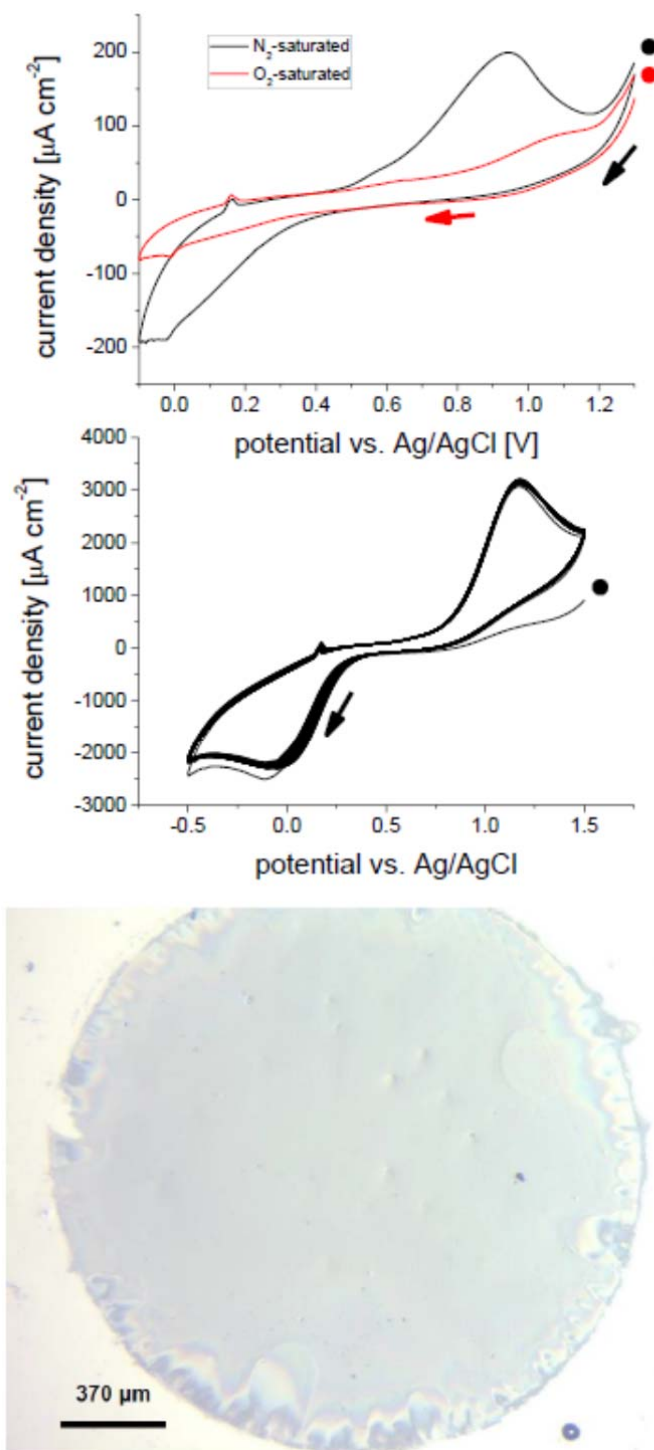


Figure S20. Pt₆/GCE *ex situ* (0.1 ML Pt). **Top:** CV of Pt₆/GCE in N₂- and O₂-saturated 0.1M HClO₄ at a scan rate of 0.1 V s⁻¹ beginning at 1.3 V vs. Ag/AgCl. 250 cycles have been performed between the N₂-saturated (black line) and the O₂-saturated case (red line), see text. **Middle:** CV (10 cycles) of Pt₆/GCE in O₂-saturated 0.1M HClO₄ at a scan rate of 0.1 V s⁻¹

beginning at 1.5 V vs. Ag/AgCl. **Bottom:** Optical micrograph of the Pt₆/GC electrode after the electrochemical measurements.

¹ S. Ranganathan, T.-C. Kuo, R. L. McCreery, **Facile preparation of active glassy carbon electrodes with activated carbon and organic solvents**, *Anal. Chem.*, **1999**, *71*, 3574-3580.

² D. T. Fagan, I.-F. Hu, T. Kuwana, **Vacuum heat treatment for activation of glassy carbon electrodes**, *Anal. Chem.*, **1985**, 2759-2763.

³ D. V. Savinova, E. B. Molodkina, A. I. Danilov, Y. M. Polukarov, **Surface and subsurface oxygen on platinum in a perchloric acid solution**, *Russ. J. Electrochem.* **2004**, *40*, 683-687.