Supporting Information Cobalt Oxide-Supported Pt Electrocatalysts: Intimate Correlation between Particle Size, Electronic Metal-Support Interaction and Stability

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1. Materials and Methods

The data presented in this study was acquired at three different experimental setups. Highresolution synchrotron radiation photoelectron spectroscopy (SRPES) coupled with an electrochemical (EC) treatment was performed at the Materials Science Beamline (MSB), Elettra-Sincrotrone Trieste (Italy). Online inductively coupled plasma mass spectrometry (ICP-MS) was carried out at the Helmholtz-Institute Erlangen-Nürnberg (Germany). The samples employed in the ICP-MS measurements were prepared in a UHV preparation chamber at the Friedrich-Alexander-University Erlangen-Nürnberg which is equipped with a dedicated transfer system. In addition, scanning tunneling microscopy (STM) images were recorded at the Charles University, Prague (Czech Republic).

1.1 Scanning Tunneling Microscopy

Experimental Setup. The morphology of the $Co_3O_4(111)$ substrate and the Pt/Co₃O₄(111) model catalysts was analyzed at a UHV setup which is operated at a base pressure of 3×10^{-10} mbar. The system comprises preparation tools, e.g. an ion gun, metal evaporators, a quartz crystal microbalance (QCM), and a low energy electron diffraction (LEED) optics, X-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM) for analysis.

Preparation of Co₃O₄(111) thin films and Pt particles. The Co₃O₄(111) thin films were prepared on Ir(100) single crystals employing adapted methods based on the procedure of Heinz and Hammer.¹⁻² We slightly modified the method with respect to the different UHV systems. For STM analysis, the Ir(100) substrate (MaTecK) was cleaned by repeating cycles of ion bombardment and annealing at 1330 K to obtain the Ir(100)-(5×1) surface structure. Annealing in O₂ (Linde 5.0, 5×10^{-7} mbar) at 1270 K yielded the Ir(100)-(2×1) oxygen terminated surface. Co (Alfa Aesar, 99.995 %) was then deposited from an electron-heated Ta crucible in a reactive oxygen atmosphere (1.5×10^{-6} mbar) at 300 K with a deposition rate of 0.7 ML/min. Here, a monolayer (ML) was defined as the vertical 4.7 Å repeat unit of the Co₃O₄(111) spinel structure. After deposition, the sample was first annealed in O₂ (2×10^{-6} mbar) at 680 K for 60 min and, subsequently, annealed in UHV at 720 K. The structure was verified by LEED and the film thickness, 5.0 nm, determined by QCM and the attenuation of the Ir 4f signal in XPS. Pt NPs were deposited by PVD of Pt (Safina, 99.99 %) at 300 K in UHV. The nominal thickness of the Pt film was determined by QCM. We prepared two samples with an amount of 0.3 and 4.5 Å Pt (0.14 and 2.05 ML).

Measurement procedure. STM measurements were performed with electrochemically etched W tips and employing sample voltages from -2 to -3 V and tunneling currents between 50 - 300 pA.

1.2 Synchrotron Radiation Photoelectron Spectroscopy Coupled with an EC Cell

Experimental setup. The MSB with a bending magnet source provided synchrotron light in the energy range of 21–1000 eV. The UHV end-station, with a base pressure of 2×10^{-10} mbar, was equipped with a multichannel electron energy analyzer (Specs Phoibos 150), a rear view LEED optics, an ion gun (Ar⁺), a gas dosing system, and two electron beam evaporators for the deposition of Co and Pt metals. Furthermore, a dedicated EC flow cell was coupled to the analysis chamber via two buffer chambers and a transfer chamber enabling a transfer of the sample between the analysis chamber and the EC cell without exposure to air.

The EC cell. The EC setup for performing ex situ emersion synchrotron radiation photoelectron spectroscopy (SRPES) at the MSB beamline is depicted in Figure S1. The EC cell was separated from the transfer chamber by a gate valve and consists of a glass housing which is divided into two compartments. The lower compartment comprises an inlet for the electrolyte, an inlet for the counter electrode (CE; Au wire, Hauner, 99.999 %), and an inlet housing the reference electrode (RE; commercial Ag/AgCl, ALS, 3 M NaCl, 0.195 V_{NHE}) which is separated from the lower compartment via a stop cock. The two compartments are connected by a capillary through which the electrolyte is pumped. The upper compartment houses an outlet for the electrolyte, a gas inlet for establishing an Ar atmosphere, and a shower for rinsing the sample with ultrapure water after the EC treatment. The electrolyte flow was controlled via inlet and outlet valves. The sample used as working electrode (WE) was mounted on a PTFE stick which is connected to a x-, y-, and z-translation stage. Potential control was established by means of a commercial potentiostat (Gamry, Reference 600).

Prior to mounting the EC flow cell to the transfer stage all glass and PTFE equipment and all metal wires were thoroughly cleaned by overnight storage in a sulfuric acid solution (98 %, Merck, EMSURE) containing NOCHROMIX (Sigma Aldrich). The equipment was rinsed with ultrapure water (MilliQ synergy UV, 18.2 M Ω cm at 25 °C, <5 ppb TOC) five times and boiled in ultrapure water three times. PFA tubes were rinsed with ultrapure water and cleaned from the outside with isopropanol.



Figure S1 Schematic drawing of the ex situ emersion SRPES setup at the Materials Science Beamline, Elettra-Sincrotrone Trieste, Italy (a). Experimental protocol before, during, and after the electrochemical treatment (b). See text for more details.

Preparation of Co₃O₄(111) thin films and Pt nanoparticles. In the following, the preparation of the oxide film at the MSB is described, based on the procedure of Heinz and Hammer.¹⁻² The Ir(100) single crystal (MaTecK, 99.99 %, depth of roughness <0.01 μ m, accuracy of orientation <0.1°) was cleaned by repetitious Ar⁺ bombardment (SIAD 6.0, 2×10⁻⁶ mbar, 1.0 kV, 300 K) and consecutive annealing cycles (UHV, 1300 K, 3 min; followed by annealing in O₂, SIAD

5.0, 1×10^{-7} mbar, 1273 K, 3 min and subsequent cooling in O₂). The Ir(100)-(5×1) reconstructed surface was obtained by annealing the sample at 1300 K in UHV. The absence of carbon or other contaminants was checked by X-ray photoelectron spectroscopy. Successive annealing of the surface at 1273 K in O₂ atmosphere (1×10⁻⁷ mbar) and cooling below 350 K in O₂ yielded the Ir(100)-(2×1)O reconstruction as confirmed by LEED. Then, cobalt (Goodfellow, 99.99 %) was deposited by physical vapor deposition (PVD) in a reactive O₂ atmosphere (2.5×10⁻⁶ mbar) at 273 K. An ordered, epitaxial film was formed by annealing in O₂ (1×10⁻⁶ mbar) at 523 K for 3 min and at 603 K for 7 min followed by subsequent annealing in UHV at 603 K for 3 min and at 680 K for another 3 min. The structure of the Co₃O₄(111) film was verified by LEED. The preparation procedure yielded films of 5.5 nm thickness as determined from the attenuation of the Ir 4f_{7/2} intensity.

Pt nanoparticles were deposited by PVD of Pt (Goodfellow, 99.99 %) at 300 K in UHV. The nominal thickness of the Pt film was determined from the attenuation of the Co 2p intensity. We prepared two samples with layer thicknesses of 3.6 Å and 0.3 Å Pt corresponding to nominal Pt monolayers (ML) of 1.64 and 0.14 ML.

Measurement procedure and data treatment. The EC measurements were carried out in 0.1 M sodium phosphate buffer (Na₂PO₄, Merck, Suprapur, 99.99 %; NaOH, Sigma Aldrich, 99.99 %) at pH 10. Prior to the start of the experiment the electrolyte was thoroughly degassed with Ar. The EC treatment was performed by establishing a constant electrolyte flow at the top of the capillary in the EC cell. Subsequently, the sample was approached to the top of the capillary under potential control and, upon contact with the electrolyte, a meniscus was formed. The sample was objected to a chosen constant potential for 3 min (0.5 – 1.5 V_{RHE}). After 3 min the sample was retracted, rinsed with degassed ultrapure water, and dried in the transfer chamber before transfer to the analysis chamber (see also Figure S1 (b)).

Core level spectra were acquired with photon energies of 180 (Pt 4f), 380 (Pt 4f), 650 (Pt 4f), and 930 eV (Co 2p). The binding energies were calibrated with respect to the Fermi level. All spectra were recorded at constant pass energy and at an emission angle of the photoelectrons of 0° with respect to the sample normal. The total spectral resolution was 200 meV (hv = 180 eV), 380 meV (hv = 380 eV), 650 meV (hv = 650 eV), and 1 eV (hv = 930 eV). All SRPES data were processed employing the KolXPD fitting software.³ The spectral components in the Pt 4f spectra were fitted with an asymmetric Doniach-Šunjić function convoluted with a Gaussian profile.

1.3 Online Inductively Coupled Plasma-Mass Spectrometry

Experimental setup. The samples for online ICP-MS experiments were prepared in a dedicated UHV preparation setup that has been described in detail elsewhere.⁴⁻⁵ Briefly, the system comprises a LEED optics, a quartz crystal microbalance, an ion gun, electron beam evaporators, a gas dosing system, and a transfer stage.

A detailed description of the online ICP-MS setup is presented in the literature.⁶⁻⁷ Briefly, an EC scanning flow cell (SFC) is coupled to an ICP-MS for the downstream analysis of dissolved species. The SFC comprises two channels which cross to form an opening enclosed by a silicon sealing to prevent leaking of the electrolyte. The inlet channel houses the counter electrode, while the reference electrode is installed downstream. The flow rate of the online ICP-MS (Perkin Elmer NexION 300X) was 205 mL min⁻¹. ¹⁸⁷Re and ⁷⁴Ge served as internal standards. The contact area of the flow cell was 0.035 cm². The sample served as working electrode, while a saturated Ag/AgCl electrode (Metrohm, 3 M KCl) and a glassy carbon rod (HTW) were used as reference and counter electrode, respectively. The potential was controlled by a commercial potentiostat (Gamry, Reference 600) and the system operated by LabVIEW routines.

Sample preparation. Co₃O₄(111) thin films were also prepared by an adapted method based on the procedure of Heinz and Hammer.¹⁻² For a detailed description of the preparation used for the online ICP-MS measurements we refer to our previous publication.⁸ Pt particles were deposited by PVD of Pt (Alfa Aesar, 99.95 %, rod of 1 mm in diameter) at 300 K. The deposition rate for Co was calibrated prior to the preparation by means of a quartz crystal microbalance. The deposition rate for Pt was calibrated prior to the preparation by means of ex situ XPS.

Measurement procedure and data treatment. The EC measurements were performed in 0.05 M sodium phosphate buffer (Na₂PO₄, Merck, Suprapur, 99.99 %; NaOH, Sigma Aldrich, 99.99 %) at pH 10. The WE was brought into contact with the SFC under potential control. Different experimental procedures were applied and the measurement protocols were repeated 2-3 times on the same sample using different spots for analysis. We mimicked the ex situ emersion SRPES procedure by applying a step potential sequence between 0.5 and 1.5 V_{RHE} (3 min per potential step). Further, we performed cyclic voltammetry (CV) between 0.5 and 1.5 V_{RHE} (5 mV/s) while we recorded the dissolution of ⁵⁹Co and ¹⁹⁵Pt. The ICP-MS data were calibrated and presented after background correction. Dissolved quantities are expressed as mass per area per time (pg cm⁻² s⁻¹). In addition, the dissolution rate is normalized to the surface atom density of Co and Pt, respectively.

2. Nanoparticle Sizes and Densities of Surface Atoms

2.1 Pt Nanoparticle Sizes and Available Surface Atoms

The density of Pt nanoparticles was obtained from the evaluation of the STM images. Taking into account the bulk density of Pt (21.45 g cm⁻³) and the nominal thickness of the Pt layer after evaporation, the average number of Pt atoms per particle could be calculated. The average number of Pt atoms per particle is related to the volume of one nanoparticle via the bulk density of Pt. Assuming a hemispherical particle shape, we calculated the average nanoparticle diameter (see Table 1). Note that a 2.05 ML Pt sample was prepared for STM, while 1.64 ML Pt were prepared for ex situ emersion SRPES and online ICP-MS. To calculate the average number of Pt atoms per particle diameter for 1.64 ML Pt, the same particle density as obtained for 2.05 ML Pt was assumed.

The number of available surface Pt atoms was calculated by subtracting the number of subsurface Pt atoms per particle, i.e. the number of Pt atoms located in the interior of a NP, from the total number of Pt atoms per particle. The number of subsurface Pt atoms in the interior of a NP was obtained by subtracting the diameter of one Pt atom ($2 \times$ the covalent radius of Pt, 136 pm) from the average nanoparticle radius. This reduced radius was then used to calculate the hemispherical volume and, consecutively, the number of Pt atoms below the layer of surface Pt atoms in the nanoparticle. Relating the number of surface Pt atoms per particle to the density of Pt particles on the surface yielded the total density of available Pt atoms at the particle surface (see Table 2). After a conversion to mass per area this value was then used to normalize the integrated online ICP-MS data. Furthermore, the Pt dispersion (surface atoms/total atoms) was calculated yielding values of 0.5 (2.05 ML Pt), 0.54 (1.64 ML Pt), and ~1 (0.14 ML Pt). Note that all parameters determined here are based on the nominal thickness of the Pt layer. As the nominal thickness of the Pt layer was calibrated by means of XPS or QCM and the same (averaged) size was assumed for all NPs, the calculated parameters can only be estimated.

Amount of deposited Pt [ML]	Nominal Pt thickness [Å]	NP density [cm ⁻²]	Average number of Pt atoms per NP	Average NP size [nm]
2.05	4.5	1×10 ¹³	~ 298	~ 2.6
1.64	3.6	1×10 ¹³	~ 238	~ 2.4
0.14	0.3	4×10 ¹³	$\sim 5-6$	~ 0.7

Table 1 Average Pt NP size calculated from the density of Pt NPs.

Amount of	Average	Average number	Average number	Density of
deposited Pt	NPsubsurface	of Pt _{subsurface} atoms	of Pt _{surface} atoms	Pt _{surface} atoms
[ML]	radius [nm]	per NP	per NP	[cm ⁻²]
2.05	~ 1.028	~ 151	~ 147	1.47×10 ¹⁵
1.64	~ 0.928	~ 111	~ 127	1.27×10 ¹⁵
0.14	~ 0.063	"0.03"	$\sim 5-6$	1.96×10 ¹⁴

 Table 2 Density of available Pt surface atoms.

2.2 Density of Co Surface Atoms

The Co₃O₄(111) film is terminated by Co atoms that would correspond to Co²⁺ in the bulk crystal (see STM image Figure 1a). The distance of Co²⁺ atoms in the surface layer equals 5.72 Å, spanning a surface unit cell of 28.3 Å².⁹ With this value, we obtain a density of surface Co²⁺ atoms of 3.5×10^{14} cm⁻². This value is also used to define 1 ML of cobalt for conversion of the Co dissolution rate between mass per area and MLs and it was employed to normalize the integrated online ICP-MS data.

3. EC Photoelectron Spectroscopy

3.1 Growth Mode of Pt Particles

Previously, we studied the stepwise growth of Pt particles on $Co_3O_4(111)$ via SRPES in detail.¹⁰⁻¹¹ Briefly, the spin-orbit doublet attributed to partially oxidized $Pt^{\delta+}$ dominated the Pt 4f spectra at low coverage. As the binding energy of $Pt^{\delta+}$ remained nearly constant, we assume that particles initially grow in form of nearly two-dimensional aggregates. Note that, in our previous studies, we did not perform depth profiling experiments. In consequence, we did not monitor the formation of Pt^{4+} species. With increasing coverage, the spin-orbit doublet of metallic Pt^0 develops and becomes the main contribution above 0.5 ML Pt. While the Pt^0 contribution increased with increasing coverage, the $Pt^{\delta+}$ signal was attenuated. This behavior indicates the formation of 3-dimensional particles with metallic Pt^0 covering the $Pt^{\delta+}$ species.

3.2 Pt Depth Profiling

In order to obtain information on the location of oxidized Pt species and, thereby, on the oxidation mechanism, we performed depth profiling experiments employing excitation energies



Figure S2 Pt 4f core level spectra of conventional Pt NPs (1.64 ML Pt) on Co₃O₄(111) before and after electrochemical exposure in 0.1 M sodium phosphate buffer at pH = 10 obtained at 180 eV (a) and 650 eV (b). Integrated peak area for the different Pt components (c). Pt⁰ marked in red, Pt^{$\delta+/2+$} in green, and Pt⁴⁺ in blue.



Figure S3 Ratios of $Pt^{\delta^{+/2+}}$ (upper panel) and Pt^{4+} (lower panel) to metallic Pt^{0} for conventional Pt NPs (1.64 ML) on Co₃O₄(111) obtained by integration of the fitted Pt 4f core level spectra.

of 180, 380, and 650 eV to record the Pt 4f core level spectra. These photon energies correspond to information depths of approximately 3.8, 5.6, and 8.2 Å, respectively.¹² The data obtained at 380 eV are presented in Figure 2 of the main letter, while the complete set of spectra recorded at 180 and 650 eV is displayed in Figure S2 for conventional NPs. Evaluation of the data by



Figure S4 Comparison of the Pt 4f core level spectra and their respective fits obtained for conventional Pt NPs (1.64 ML) after preparation (left panel) and after EC treatment at 1.5 V_{RHE} .

peak integration gives the ratios of oxidized Pt^{4+} and $Pt^{\delta+}$ or Pt^{2+} to metallic Pt^{0} , respectively, which are presented in Figure S3. Before applying oxidizing potentials, the ratio of oxidized to metallic Pt species is nearly independent of the excitation energy. Only at the highest potential, i.e. 1.5 V_{RHE}, a large difference is observed (see also Figure S4 comparing the Pt 4f spectra of the UHV prepared sample and after emersion at 1.5 V_{RHE}). With decreasing excitation energy, the ratio of oxidized to metallic Pt species increases. That means that the ratio shifts in favor of the oxidized species at the most surface sensitive, lowest excitation energy. This behavior is in line with the formation of PtO and PtO₂ surface oxides at increasing potentials.¹³⁻¹⁴

In Figure S5 we show the Pt 4f spectra recorded with photon energies of 180 and 650 eV for subnanometer Pt aggregates. Peak integration gives the ratio of Pt^{4+} species to partially oxidized $Pt^{\delta+}$ or Pt^{2+} species that is presented in Figure S6. While the data obtained at 180 eV is difficult to fit due to the high level of noise (see Figure S6 (b)), a trend is nevertheless visible: The ratio of fully oxidized Pt^{4+} to partially oxidized $Pt^{\delta+}$ is always lowest at the lowest, most surface sensitive photon energy. This implies that Pt^{4+} species are located and, especially at oxidizing potentials, also formed in the subsurface region of the model electrocatalyst.



Figure S5 Pt 4f core level spectra of subnanometer Pt aggregates (0.14 ML Pt) on $Co_3O_4(111)$ before and after electrochemical exposure in 0.1 M sodium phosphate buffer at pH = 10 obtained at 180 eV (a) and 650 eV (b). Integrated peak area for the different Pt components (c). Pt⁰ marked in red, Pt^{δ^+} in green, and Pt^{4^+} in blue.



Figure S6 Ratios of Pt^{4+} to partially oxidized $Pt^{\delta+}$ for subnanometer Pt aggregates (0.14 ML) on Co₃O₄(111) obtained by integration of the fitted Pt 4f core level spectra (a). Comparison of the Pt 4f core level spectra and their respective fits obtained for subnanometer aggregates (0.14 ML) after preparation (left panel) and after EC treatment at 1.5 V_{RHE} (b).

3.3 Total Intensity of the Pt 4f Signal

While the loss of total intensity in a measurement performed purely in ultrahigh vacuum can indicate NP sintering,¹¹ the present study is more complex. Contamination due to electrolyte exposure and dissolution processes need to be considered. The total integrated intensity of all Pt 4f spectra at all excitation energies is plotted in Figure S7. The intensity of the Pt 4f signal drops significantly after the first exposure to electrolyte. After the following EC treatments, the intensity of the Pt 4f signal still decreases, but the decrease is weaker than after the first EC treatment. This behavior is expected considering that residues from the electrolyte as well as additional contaminations can cover the sample regardless of the thorough rinsing with



Figure S7 Total integrated intensity of the Pt 4f core level spectra for subnanometer Pt aggregates (upper panel) and conventional Pt NPs (lower panel) as compared to the integrated intensity of the C 1s core level spectra (hv = 380 eV). The intensity of the C 1s signal (black line) was mirrored and scaled to give the orange fit for the Pt 4f intensity at 380 eV.

ultrapure water before transfer to the analysis chamber.¹⁵ The signal of the buffer, e.g. in the P 2p core level spectra, however, is comparatively low. The strongest signal is observed in the C 1s core level spectra.

The integrated intensity of the C 1s spectra is included in Figure S7. The line following the evolution of the C 1s signal was copied, mirrored, and scaled to the integrated intensity of the Pt 4f signal obtained at 380 eV. As the Pt 4f signal only deviates slightly from the mirrored C 1s signal, the damping of the Pt 4f signal is directly coupled to carbonaceous deposits on the

sample. Carbonaceous deposits most likely stem from contaminations in the UHV buffer chambers during transfer. After the last emersion at 0.5 V_{RHE} , we estimate the atomic ratio of Pt compared to the amount of carbon. We calculate 1 and 10 % of Pt for subnanometer and conventional Pt particles and estimate a theoretical carbon layer thickness of 15 and 10 Å, respectively. Here, possible contributions to the loss in the signal intensity of Pt 4f spectra due to Pt dissolution cannot be entirely excluded but are further studied and discussed via online ICP-MS experiments.

3.4 Oxidation and Reduction of the Co₃O₄(111) Support – Evaluation of Co 2p Core Level Spectra and Resonant Photoemission Spectroscopy

In order to understand how much the oxide support is involved in the EC oxidation of Pt NPs, i.e. to assess the extent of electronic metal-support interactions and oxygen spillover processes, we analyzed the degree of reduction of the $Co_3O_4(111)$ thin film by means of XPS, SRPES, and resonant photoemission spectroscopy (RPES). We recorded Co 2p core level and valence band spectra not only for the Pt/Co₃O₄(111) samples but also for a Co₃O₄(111) reference sample that was subjected to the same electrochemical measurement protocol (see Materials and Methods). The presence of Pt⁴⁺ species after deposition of low amounts of Pt is striking and, to the best of our knowledge, has not been observed before on Co₃O₄(111). To elucidate the influence of the support, we compare the Co 2p core level spectra obtained by SRPES and valence band spectra



Figure S8 Comparison of the Co 2p core level spectra (left panel) and the valence band spectra (right panel) of the pristine $Co_3O_4(111)$ support (top) and after deposition of subnanometer Pt aggregates (bottom) to evaluate the degree of reduction of the $Co_3O_4(111)$ film.

for RPES analysis of the $Co_3O_4(111)$ thin film before and after deposition of 0.3 Å of Pt (0.14 ML Pt) in Figure S8.

Despite the complexity of the spectral contributions in the Co 2p core level spectra, it is possible to fit SRPES spectra of Co₃O₄ at low degrees of reduction.¹⁶ The employed fitting procedure has been reported earlier and the degree of reduction is given as the Co³⁺/Co²⁺ ratio obtained from the integrated intensity of the main contributions for Co³⁺ and Co²⁺ identified at 779.5 and 781.3 eV, respectively.^{11, 16}

For analysis of the RPES data, we followed a procedure reported earlier.¹⁶ We chose selected valence band spectra at different photon energies corresponding to the strongest resonances in Co^{3+} (~ 781.0 eV), Co^{2+} (1.4 eV below the Co^{3+} resonance), and an off-resonance spectrum (773.0 eV) and determined the resonant enhancement ratio (RER). The RER is given by the $D(Co^{3+})/D(Co^{2+})$ ratio, where $D(Co^{3+})$ corresponds to the difference in intensity of the Co^{3+} and Co^{2+} resonance spectra at a binding energy of ~2.0 eV and $D(Co^{2+})$ is defined as the maximum difference in intensity between the Co^{2+} and off-resonance spectra between 4-5 eV. Employing the reported calibration, the RER yields the Co^{3+}/Co^{2+} ratio after multiplication by a factor of 2.2.¹⁶

After deposition of subnanometer Pt aggregates, the Co^{3+}/Co^{2+} ratio is reduced from 2.02 to 1.94 as determined by SRPES or from 1.70 to 1.69 as given by RPES. These values correspond to changes in the Co^{3+}/Co^{2+} ratio of 4.2 and 0.6 %, respectively. To put these values in relation with the presence of oxidized Pt NPs and the extent of electronic metal-support interactions, we calculate how much the Co^{3+}/Co^{2+} ratio should decrease when all Pt that is present as Pt⁴⁺ species would transfer its charge to Co^{3+} atoms reducing them to Co^{2+} atoms (see also Table 3).

Amount of deposited Pt [ML]	Nominal Pt thickness [Å]	Density of Pt atoms [cm ⁻²]	Density of Pt ⁴⁺ species [cm ⁻²]	Charge per area [cm ⁻²]
0.14	0.3	7.56×10 ¹⁸	1.55×10 ¹⁸	6.2×10^{18}
3×λ [Å]	Density of Co ²⁺ in 3×λ [cm ⁻²]	Density of Co ³⁺ in 3×λ [cm ⁻²]	Density of Co ²⁺ after charge transfer [cm ⁻²]	Density of Co ³⁺ after charge transfer [cm ⁻²]
16.5	1.46×10^{20}	2.92×10 ²⁰	1.52×10^{20}	2.86×10 ²⁰

Table 3 Estimation of the $Co_3O_4(111)$ reduction upon charge transfer at Pt^{4+} formation in UHV.

First, we calculate the total density of Pt atoms upon depositing a nominal layer of 0.3 Å by taking into account the bulk density of Pt (21.45 g/cm³). The ratio of the integrated peak areas in the Pt 4f core level spectrum after deposition (Pt⁴⁺, 20.5 %) gives the density of Pt⁴⁺ species per area. The amount of charge that could be transferred to the support is four times as large as the density of Pt⁴⁺ species.

Next, we correlate the amount of charge with the reduction of the $Co_3O_4(111)$ thin film. For simplicity, we assume that the information depth of the Co 2p spectra stems from $3 \times \lambda$, the inelastic mean free path of Co 2p photoelectrons (0.55 nm), and that charge is solely transferred into this region.¹¹ Considering the bulk density of Co_3O_4 (6.11 g/cm³) and its stoichiometry we obtain a density of Co^{3+} or Co^{2+} atoms per area in the top layer (thickness of $3 \times \lambda$). Subtracting the amount of charge per area obtained through formation of Pt⁴⁺ species from the Co³⁺ density and adding it to the Co²⁺ density gives the new density of Co³⁺ and Co²⁺ atoms and the corresponding Co³⁺/Co²⁺ ratio in the reduced oxide film. The new Co³⁺/Co²⁺ ratio of 1.88 corresponds to a change of 6.1 % and neglects further reduction by possible charge transfer from Pt to Co³⁺ to form Pt⁸⁺ or Pt²⁺ species. If this additional charge transfer was considered,



Figure S9 Co 2p core level spectra obtained with an Al K α source (hv = 1486.6 eV, left) and synchrotron radiation (hv = 930 eV, middle) and valence band spectra (right) of a Co₃O₄(111) thin film before and after EC treatment in 0.1 M sodium phosphate buffer at pH = 10.



Figure S10 Co 2p core level spectra obtained with an Al K α source (hv = 1486.6 eV, left) and synchrotron radiation (hv = 930 eV, middle) and valence band spectra (right) of subnanometer Pt aggregates on a Co₃O₄(111) thin film before and after Pt deposition and after EC treatment in 0.1 M sodium phosphate buffer at pH = 10.

the $\text{Co}^{3+}/\text{Co}^{2+}$ ratio would be even lower and the change greater ($\text{Co}^{3+}/\text{Co}^{2+}$ at 1.67, change of 16.6 % upon additional formation of 79.5 % Pt²⁺). As such a great change in the $\text{Co}^{3+}/\text{Co}^{2+}$ ratio is neither observed in the SRPES nor in the RPES data, it is unlikely that all charge is transferred to the upper support layers only.

In Figure S9 and S10 we provide all Co 2p core level spectra and valence band spectra obtained for Co₃O₄(111) and 0.3 Å Pt/Co₃O₄(111) after preparation in UHV and after the EC treatment. The evaluated data is partially summarized in Figure S11. Here, we compare the Co³⁺/Co²⁺ ratio obtained from the analysis of the SPRES and RPES data as described above dependent on the respective sample treatment. The scattering of the data points shows that elucidating the degree of reduction for Co₃O₄ is not facile. With the lines in the graph we try to provide a guide-tothe-eye and pinpoint some general trends. Upon immersion at 0.5 V_{RHE} the Co₃O₄(111) thin film is slightly reduced. The same behavior is observed for the Pt/Co₃O₄(111) sample. With increasing potentials Co₃O₄(111) is reoxidized, only to be slightly reduced again upon returning



Figure S11 Comparison of the degree of reduction of a $Co_3O_4(111)$ thin film before and after EC treatment without (left) and with subnanometer Pt particles deposited on (right).

to the initial potential of $0.5 V_{RHE}$. The Co₃O₄ support itself is dynamically oxidized and reduced under potential control. The Pt/Co₃O₄(111) sample follows the same trends. Hence, it is not easy to relate changes in the Co³⁺/Co²⁺ ratio to charge transfer or oxygen spillover processes between subnanometer Pt aggregates and the support, when oxygen can also be supplied by the electrolyte and interacts with the support in the same potential window.

3.5 EC Data

While exposing the samples to the electrolyte under potential control, we also recorded the current response to exclude substantial errors stemming from the EC treatment. The data are



Figure S12 Current responses of $Co_3O_4(111)$, conventional Pt NPs on $Co_3O_4(111)$, and subnanometer Pt aggregates on $Co_3O_4(111)$ during exposure to 0.1 M sodium phosphate buffer (pH = 10) at constant potential. In the right panel the minimum (hollow symbols) and maximum (full symbols) respective peak currents are shown.

presented in Figure S12. Small current spikes are attributed to short disruptions, e.g. movement close to the experimental setup.

At 0.5 V_{RHE} negative, reductive currents are recorded. Starting from 0.7 V_{RHE} only positive, increasingly oxidative currents are observed. These current responses corroborate the photoelectron spectroscopic results on the oxidation state of the metal oxide support film, which is reduced at 0.5 V_{RHE} and reoxidized at increasing potentials. Comparing the three samples, strong deviations in the current flow are only observed at the lowest potential.

4. Current Responses and Potential-Dependent Evaluation of the online ICP-MS Measurements

In this section we provide complementary data on the current that was recorded during the online ICP-MS measurements, see Figure S13. Additionally, Figure S13 again contains the dissolution rates for Pt (middle) and Co (bottom) in a direct comparison of the samples and employing different scales.

In the first experiment that mimics the experimental procedure of the ex situ emersion SRPES, a negative, cathodic current is recorded for all three samples upon contact at 0.5 V_{RHE} . Stepping the potential up then results in positive, anodic currents. This behavior fits well to the current response obtained in ex situ emersion SRPES. The only difference is observed in the cathodic current at 0.5 and 0.7 V_{RHE} which is strongly enhanced in the online ICP-MS measurement for conventional NPs. Similar increased cathodic currents are also recorded during the CV procedure for conventional NPs below 0.9 V_{RHE} . This behavior is attributed to the oxygen



Figure S13 Complementary online ICP-MS data for the step potential procedure (left) and the CV measurement (right) in 0.05 M sodium phosphate buffer at pH = 10. Current responses are shown in the top panel. The Pt dissolution rate is presented in the middle and the Co dissolution rate in the bottom. The results for Co₃O₄(111) are marked in black, conventional Pt NPs on Co₃O₄(111) in blue, and subnanometer Pt aggregates on Co₃O₄(111) in orange.

reduction reaction at Pt which is typically reported to start below 0.9 V_{RHE} .¹⁷ Note that small leakages could not be avoided while performing the online ICP-MS experiments for conventional NPs due to a slight curvature of the Ir(100) single crystal. Consequently, the presence of oxygen is not surprising and could not be avoided completely.

When the potential is increased during the step protocol dissolution of Pt is observed as small peak at 0.9 V_{RHE} and above at every consecutive step for conventional NPs on Co₃O₄(111). In the CV, two anodic peaks are recorded indicating the dissolution of Pt at conventional NPs. Here, dissolution starts roughly at 0.8 V_{RHE} and increases again at 1.1 V_{RHE} . These values are in fair agreement with literature and are attributed to the transient dissolution of Pt during the formation of PtO and PtO₂ in alkaline media, respectively.¹⁸⁻¹⁹ Further contributions to the second anodic peak can stem from surface processes and changes in the oxidation state during the onset of the oxygen evolution reaction.¹⁸

Anodic dissolution of Pt is not observed for subnanometer aggregates. On the contrary, the dissolution rate of Pt only levels off completely above 1.1 V_{RHE} in the case of subnanometer NPs. A similar behavior is observed for the Co dissolution. Whereas cobalt dissolution is negligible during the step protocol on $Co_3O_4(111)$ and for conventional NPs on $Co_3O_4(111)$, enhanced cobalt dissolution only completely stops at 1.1 V_{RHE} for subnanometer aggregates. During the CV, the drop in the Co dissolution rate coincides on all samples at $0.8 - 0.9 V_{RHE}$ during the anodic scan but is most pronounced for subnanometer aggregates.

The CV data is analyzed in more detail in Figure S14. Here, we plot the current and dissolution rate dependent on the potential with a special emphasis on the dissolution during the reverse, cathodic scan. Note that in the right panel adjacent data points were averaged to reduce the amount of noise in the dissolution data. It is noteworthy that the cathodic dissolution of Pt starts at 1.1 V_{RHE} irrespective of the NP size. Cathodic dissolution is attributed to the reduction of platinum oxide and results from place-exchange processes.²⁰ When we compare the Co dissolution during the cathodic scan, we observe the following. On the pristine Co₃O₄(111) support and for conventional NPs Co dissolution starts at 0.9 V_{RHE} and increases linearly. For subnanometer NPs, on the other hand, the dissolution rate of Co increases earlier (~ 1.1 V_{RHE}) and more rapidly and closely resembles the dissolution curve of Pt.



Figure S14 Potential-dependent representation of the CV measurements obtained with the online ICP-MS. Current response (top), Pt dissolution (middle), and Co dissolution (bottom) for $Co_3O_4(111)$ (black), conventional Pt NPs on $Co_3O_4(111)$ (blue), and subnanometer Pt aggregates on $Co_3O_4(111)$ (orange). In the left panel, the complete data is shown, while the right panel contains a zoom of the CV and the return-scan for the dissolution data.

While stepping up the potential, as well as during the cathodic potential scan, the dissolution rates of Pt and Co behave similarly in the case of subnanometer NPs. Hence, we conclude that both processes are related. The results are connected to the ex situ emersion SRPES results in the main letter and discussed therein.

In a last note we comment on the CV obtained during the online ICP-MS experiments. For the pristine $Co_3O_4(111)$ support we observe a broad peak at 1.3 V_{RHE} both, in the anodic and cathodic scan. This peak is attributed to the oxidation of Co_3O_4 spinel to CoOOH and in line with literature where Reikowski et al. reported the reversible formation of a CoOOH skin layer on $Co_3O_4/Au(111)$.²¹ For subnanometer Pt aggregates this peak is strongly enhanced indicating an increased redox activity.

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