Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Anisotropy of Pt Nanoparticles on Carbon- and Oxide-Support and Their Structural Response to Electrochemical Oxidation Probed by In-situ Techniques

Henrike Schmies[1,‡], *Arno Bergmann*[1,◊,‡], *Elisabeth Hornberger*[1], *Jakub Drnec*[2], *Guanxiong Wang*[3], *Fabio Dionigi*[1], *Stefanie Kühl*[1], *Daniel J.S. Sandbeck*[4], *Serhiy Cherevko*[4], *Vijay Ramani*[3], *Karl J.J. Mayrhofer*[4], *Peter Strasser*[1*]

‡ These authors contributed equally to this work.

[1] Department of Chemistry, Chemical Engineering Division, Technical University of Berlin, Berlin, Germany

[2] European Synchrotron Radiation Facility (ESRF), Grenoble, France

[3] School of Engineering & Applied Science, Washington University in St. Louis, St. Lois, USA

[4] Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IEK-11), Forschungszentrum Jülich, Erlangen, Germany

◊ Present address: Fritz-Haber-Institute of the Max-Planck-Society, Department of Interface Science, Faradayweg 4-6, 14195 Berlin, Germany

*Email: pstrasser@tu-berlin.de

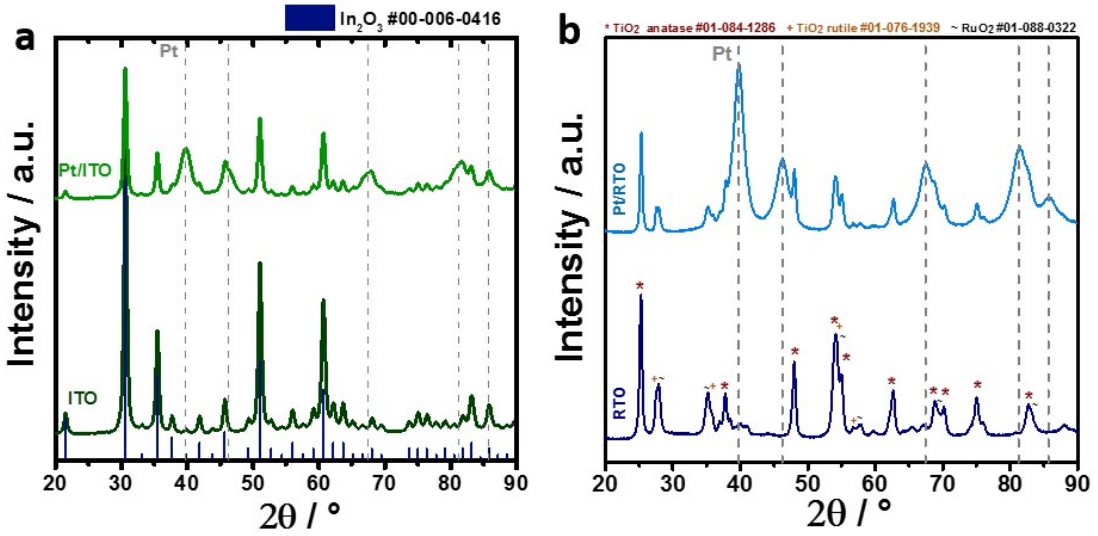

Figure S1 X-ray diffractograms of (a) ITO and Pt/ITO with solid blue lines indicating In_2O_3 reference pattern and (b) RTO and Pt/RTO with symbols indicating TiO_2 anatase and rutile and RuO_2. Vertical dashed lines denote reference powder diffraction patterns of fcc Pt (PDF#00-004-0802). XRDs were obtained using Cu K_α radiation.

Table S1 Pt weight loading (wt%) for Pt on ITO, RTO and C as determined by ICP-OES analysis.

Pt loading	wt%
Pt/C	20.0
Pt/ITO	29.9
Pt/RTO	43.1

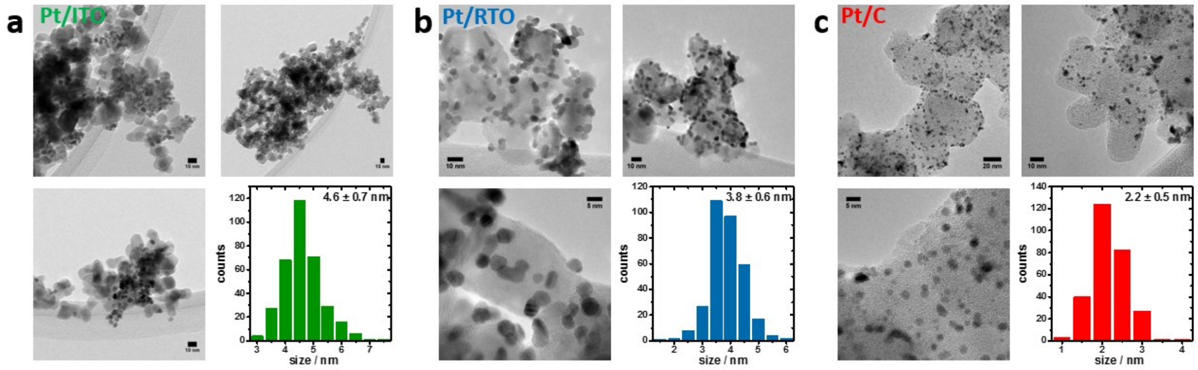

Figure S2 Morphology of Pt nanoparticles on a) ITO (green), b) RTO (blue) and c) carbon (red) support and corresponding histograms showing mean particle diameter as determined by transmission electron microscopy. The particle size histogram was determined from analyzing > 200 particles along their shortest particle axes.

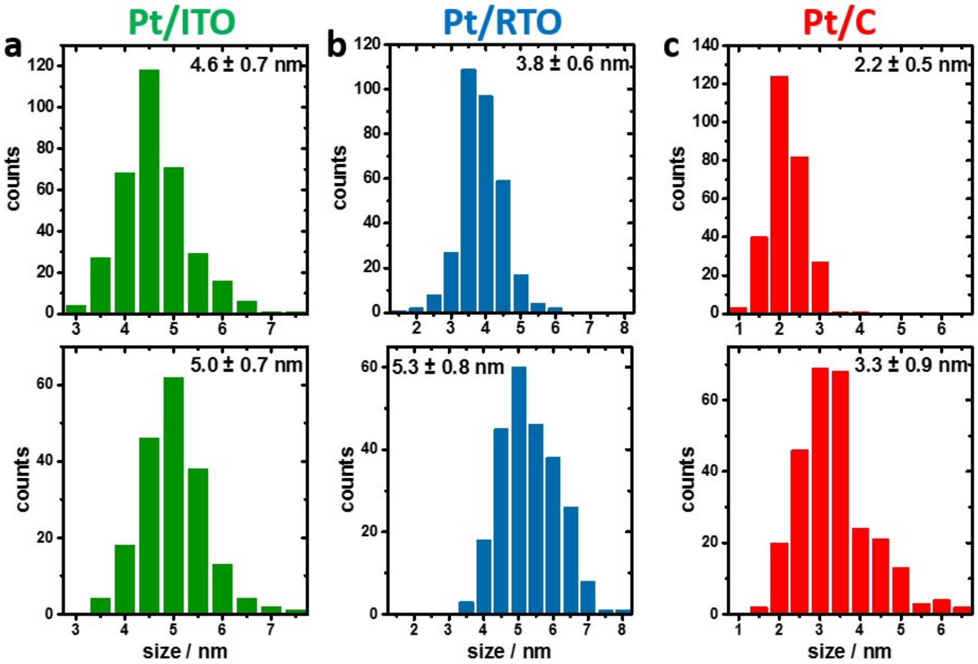

Figure S3 Histograms of mean particle diameter for Pt supported on (a) ITO (green), (b) RTO (blue) and (c) carbon (red) support. Top row shows the average particle diameter measured along their shortest particle axis and bottom row along their longest particle axes.

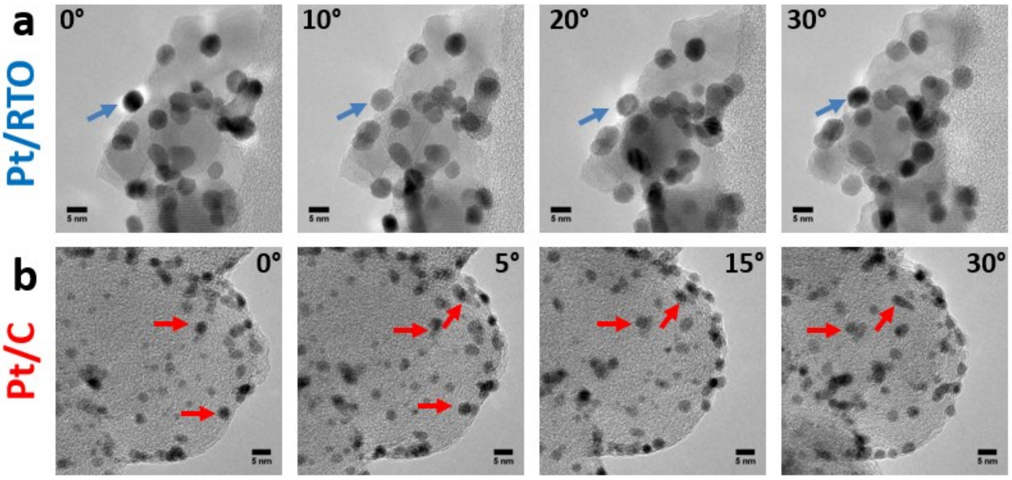

Figure S4 Morphology of Pt nanoparticles on a) RTO (blue) and b) carbon (red) support in a TEM tilting study form 0-30°.

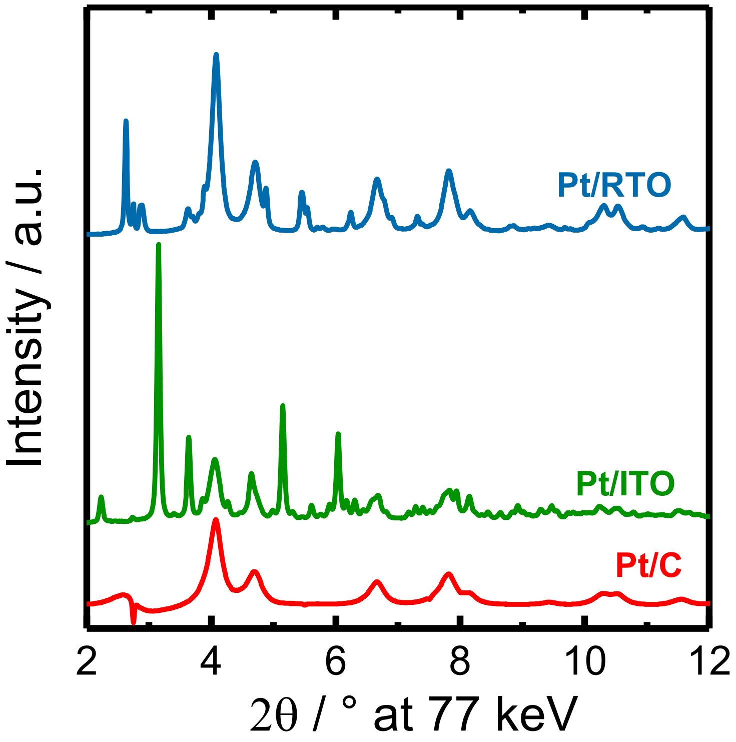

Figure S5 High energy XRD patterns of Pt/RTO (blue), Pt/ITO (green) and Pt/C (red) in the as-prepared state.

Table S2 Crystallite diameter (D_x, D_y and D_z) for ellipsoidal Pt particles on RTO and C support and for spherical particles on ITO as determined by Rietveld refinement of HE-XRD.

	crystallite diameter / nm		
	D_x	D_y	D_z
Pt/ITO	4.06±0.09		
Pt/RTO	3.28±0.05	4.54±0.11	2.44±0.02
Pt/C	2.32±0.04	2.46±0.05	1.78±0.02

Table S3 Structural parameters of Pt on ITO, RTO and C: O_{td}-incorporation and lattice constant by Rietveld refinement of HE-XRD.

	O_{td}-incorporation	lattice parameter a_{Pt} / Å
Pt/ITO	0.15±0.02	3.9301
Pt/RTO	0.000±0.016	3.9199
Pt/C	0.000±0.018	3.9136
Pt bulk	-	3.9231

Table S4 Comparison of ECSA values based on the integration in the H_{upd} region or the CO Oxidation peak area.

ECSA/ m^2 g_{Pt}^{-1}	H_{upd}	CO
Pt/C	63.1	67.5
Pt/ITO	17.8	25.6
Pt/RTO	19.0	16.7

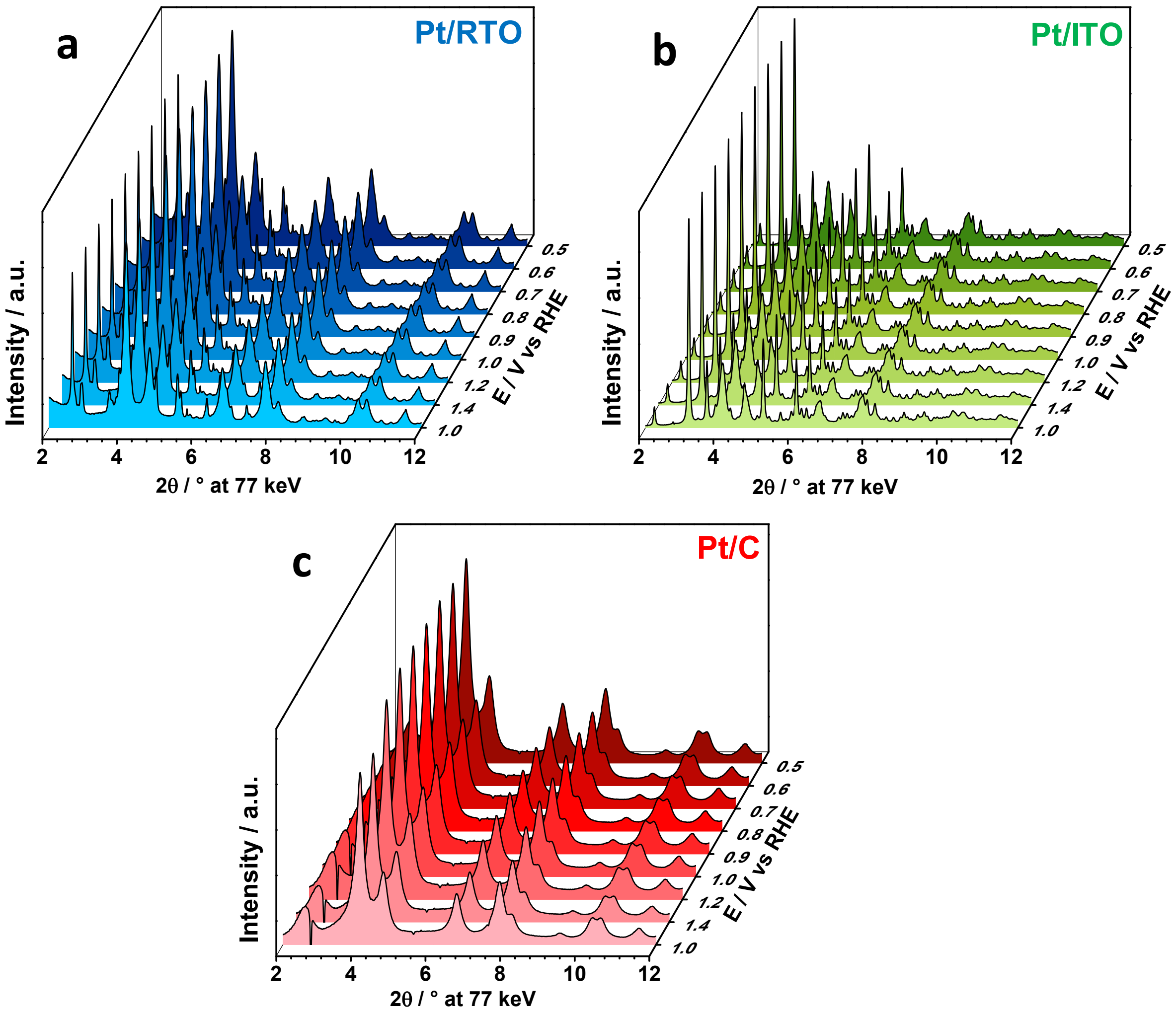

Figure S6 *In situ* high-energy X-ray diffraction patterns of Pt nanoparticles supported on ITO (green, a), RTO (blue, b) and carbon (red, c) as recorded during the electrochemical oxidation of Pt.

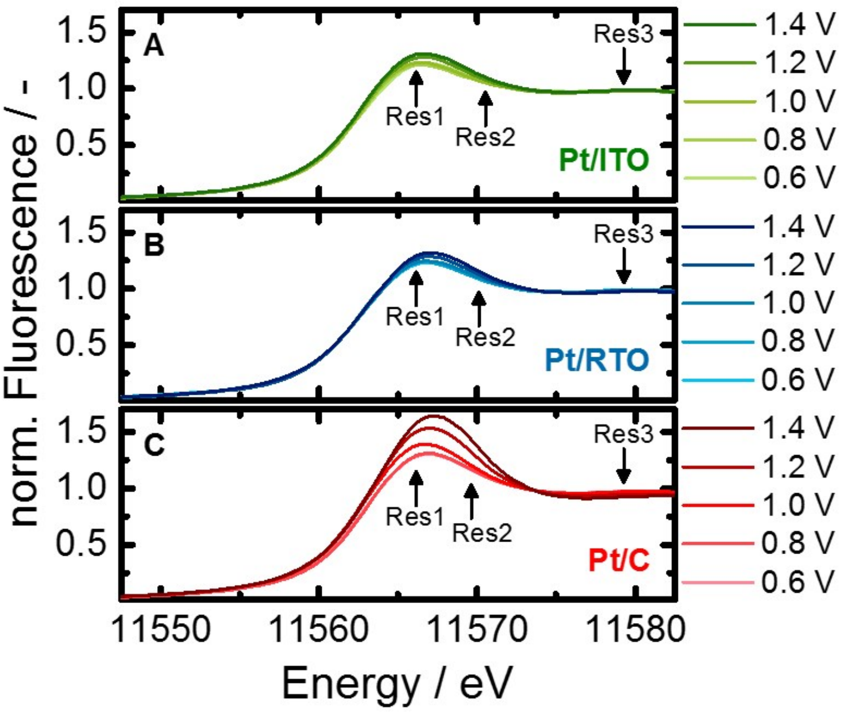

Figure S7 Normalized *in situ* Pt L_3–edge X-ray near-edge absorption spectra for Pt nanoparticles supported on ITO (green, a), RTO (blue, b) and carbon (red, c) for potentials from 0.6 – 1.4 V of electrochemical oxidation of Pt. The positions of the Pt L_3 resonances applied in the fit procedure are denoted.

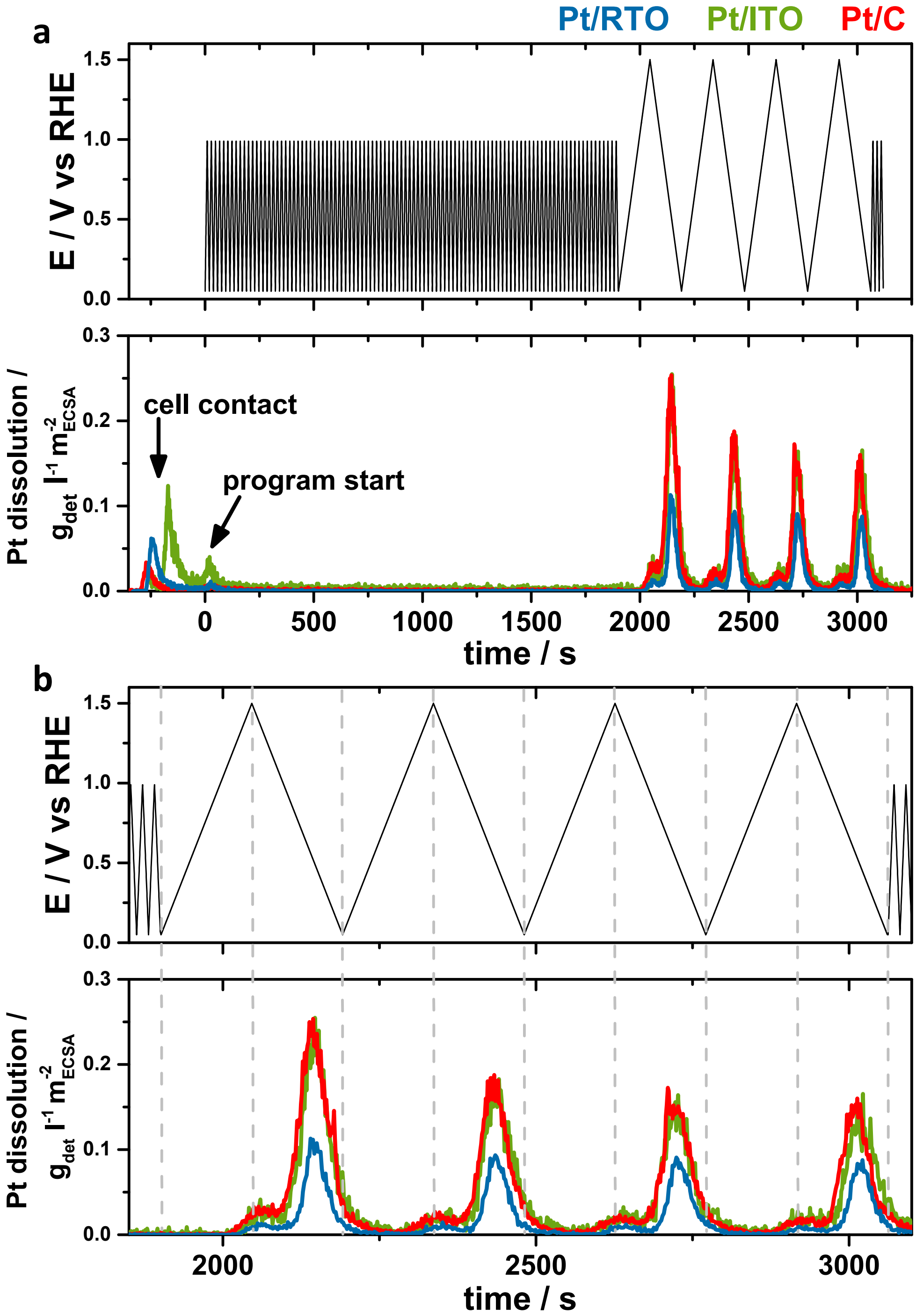

Figure S8 H_{upd}-ECSA-normalized Pt dissolution profiles from *in situ* SFC-ICP-MS measurement in g_{det} Pt per volume electrolyte in l and electrochemical surface area (ECSA) in m^2_{ECSA}. a) shows the whole electrochemical measurement (100 CVs of activation and 4 CVs of Pt Oxidation from 0.05 – 1.5 V) and the corresponding dissolution profiles for Pt on carbon (red), ITO (green) and RTO (blue) support and b) the four oxidation cycles from 0.05-1.5 V. Cell contact and program start are marked with arrows.

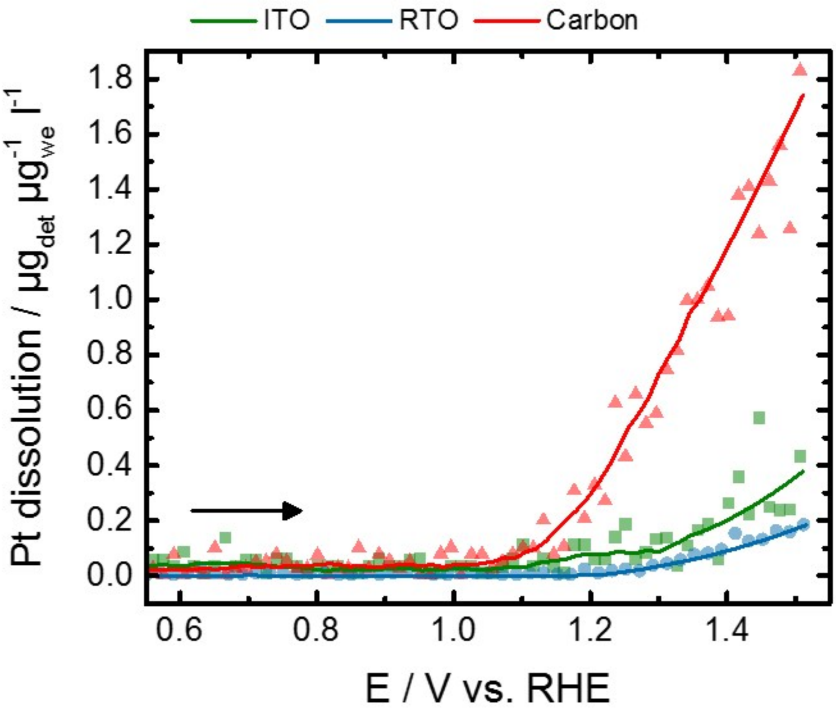

Figure S9 Evolution of mass-normalized Pt dissolution rate as determined by SFC-ICP-MS measurements during the initial anodic potential sweep from 0.05-1.5 V for Pt nanoparticles supported on ITO (green), RTO (blue), and carbon (red).

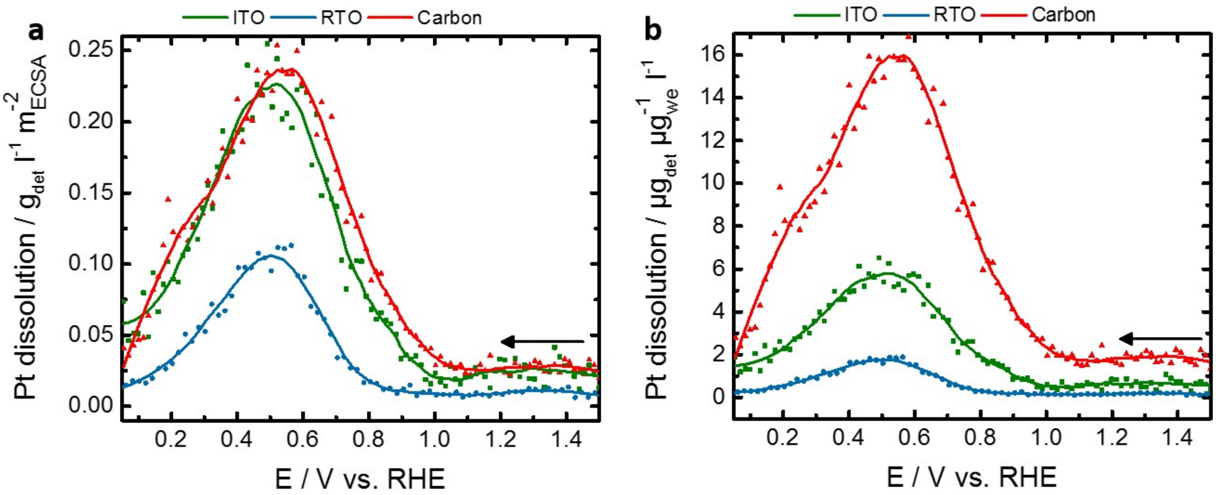

Figure S10 H_{upd}-ECSA-normalized (a) and mass-normalized (b) Pt dissolution rate of electrochemically-oxidized Pt nanoparticles supported on ITO (green), RTO (blue), and carbon (red) as determined by SFC-ICP-MS measurements during the cathodic potential sweep from 1.5-0.05 V after initial anodic potential sweep up to 1.5 V.