

Supporting Information

Tuning the Pt-Co nanoparticle motifs for enhancing the HOR performance in alkaline media

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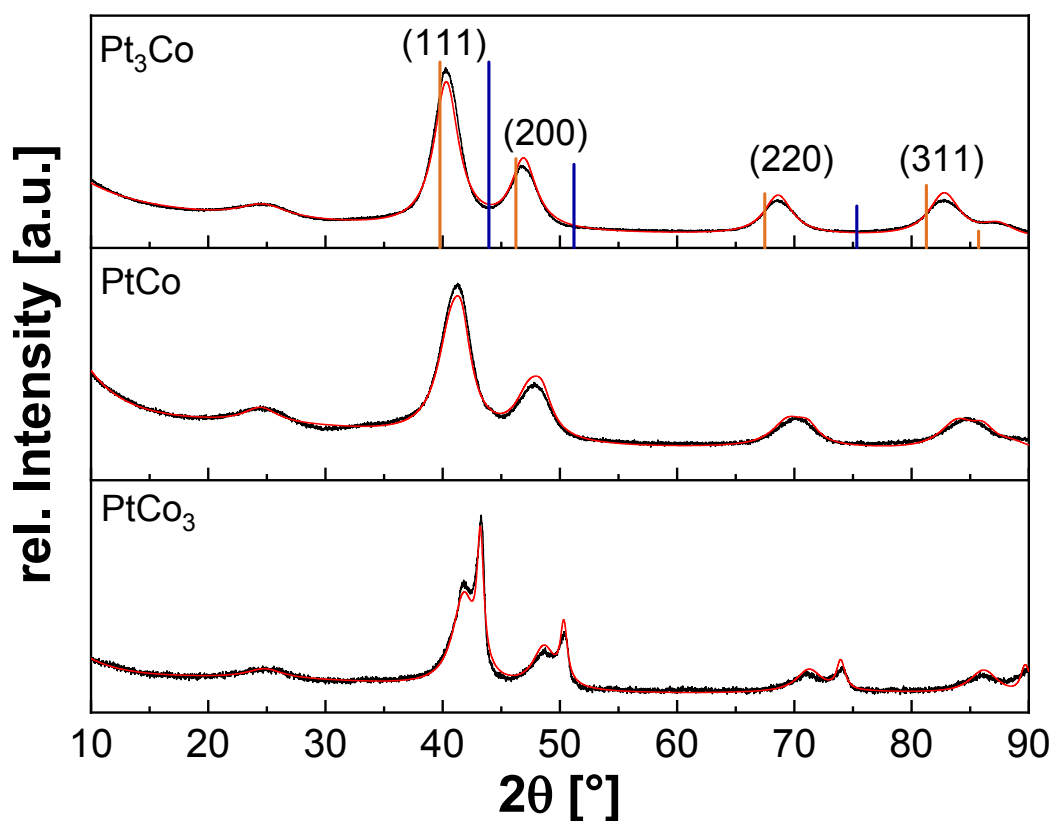


Figure S1. XRD profiles of pristine Pt_xCo_{1-x} catalysts prepared by wet-impregnation – freeze drying – annealing process. Rietveld profile fits of the diffraction data for Pt_3Co ($R_{wp} = 3.93$), $PtCo$ ($R_{wp} = 2.02$) and $PtCo_3$ ($R_{wp} = 1.26$) are denoted with red line. The results from the Rietveld quantification and lattice parameters are summarized in Table S1. Vertical orange and blue lines denote reference patterns for pure face-centered cubic (fcc) Pt (card no. 00-004-0802) and pure fcc Co (card no. 00-015-0806) obtained from the International Center for Diffraction Data (ICDD).

Table S1. Crystal structures, lattice parameters, crystallite sizes, results from Rietveld quantification, and stoichiometric compositions of pristine Pt_xCo_{1-x} alloy nanoparticles prepared by wet-impregnation – freeze drying – annealing process. The quality of the fit from Rietveld quantification analysis is given by R -weighted pattern (R_{wp}).

	space group	lattice parameter [Å]	crystallite size [nm]	Rietveld quantification [wt.%]	composition via Vegard's law	R_{wp}
Pt_3Co	Fm-3m	3.863 ± 0.002	3.4 ± 0.1	100	$Pt_{84}Co_{16}$	3.93
$PtCo$	Fm-3m	3.819 ± 0.002	2.9 ± 0.1	69.8 ± 0.5	$Pt_{73}Co_{27}$	2.02
	Fm-3m	3.740 ± 0.002	4.6 ± 0.1	30.2 ± 0.5	$Pt_{52}Co_{48}$	
$PtCo_3$	Fm-3m	3.743 ± 0.002	3.7 ± 0.1	61.6 ± 0.5	$Pt_{53}Co_{47}$	1.26
	Fm-3m	3.624 ± 0.002	13.2 ± 0.5	38.4 ± 0.5	$Pt_{21}Co_{79}$	

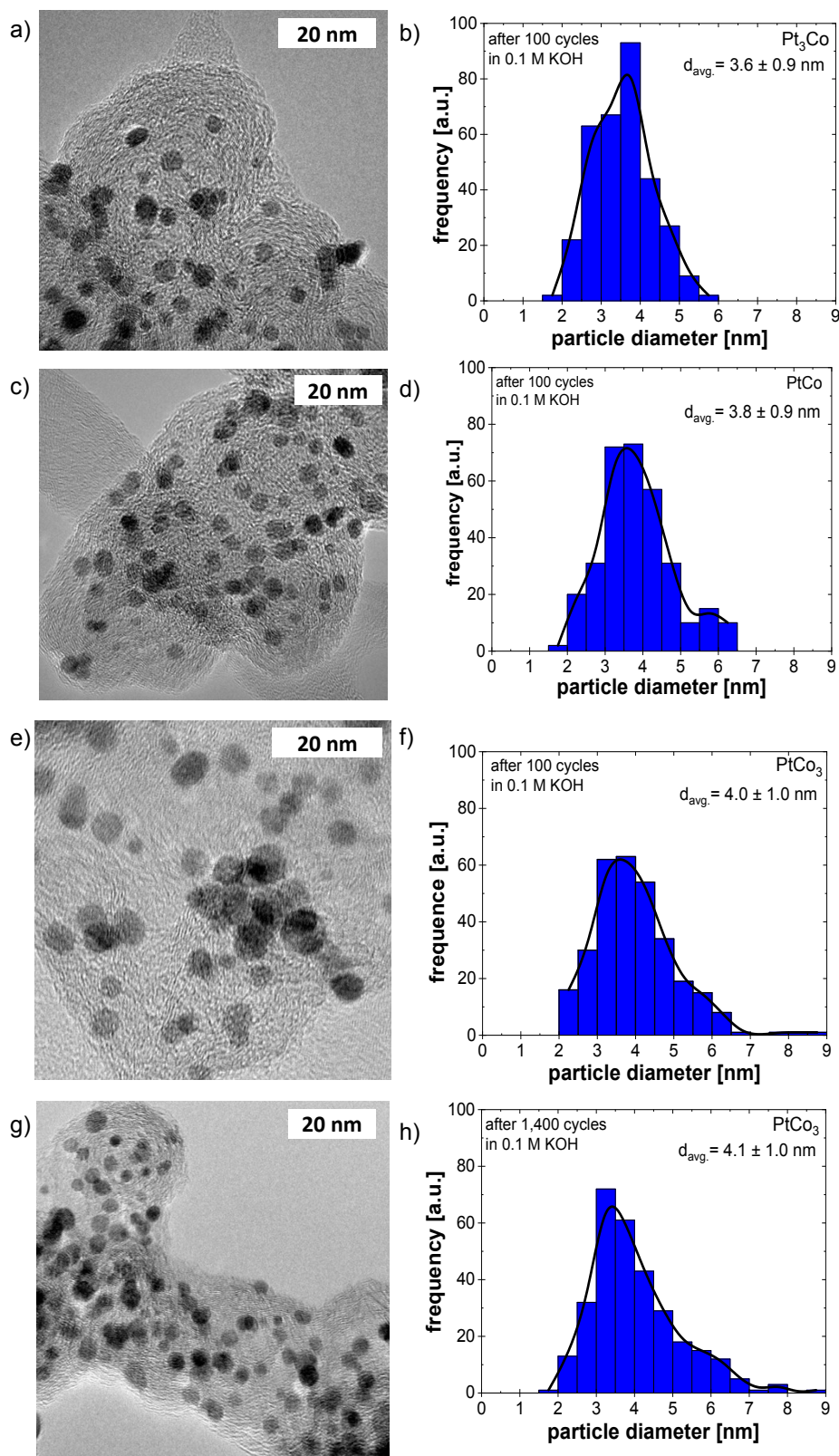


Figure S2. High-resolution TEM micrographs and particle size distributions for Pt_3Co (a, b), $PtCo$ (c,d), and $PtCo_3$ (e,f) after dealloying and surface re-arrangement induced by 100 potential cycles in 0.1 M KOH. No changes in particle size distribution are observed for Co-segregated $PtCo_3$ core-shell catalysts even after 1,400 cycles (g, h). By comparing Figure 1 of the main manuscript, the mean particle sizes of pristine and electrochemically treated Pt_xCo_{1-x} nanoparticles remained unchanged in the respective error range. The scale bar for all HR-TEM micrographs is 20 nm, respectively.

Table S2. Experimental acquisition parameters like pass energy, number of scans, dwell time, and energy step size for XPS investigations on Pt_xCo_{1-x} catalysts.

XPS line	pass energy [eV]	number of scans [a.u.]	dwell time [ms]	energy step size [eV]
survey	100	10	10	1
Pt 4f	10	80	50	0.02
C 1s	10	10	50	0.02
O 1s	10	10	50	0.02
Co 2p	100	200	50	0.1

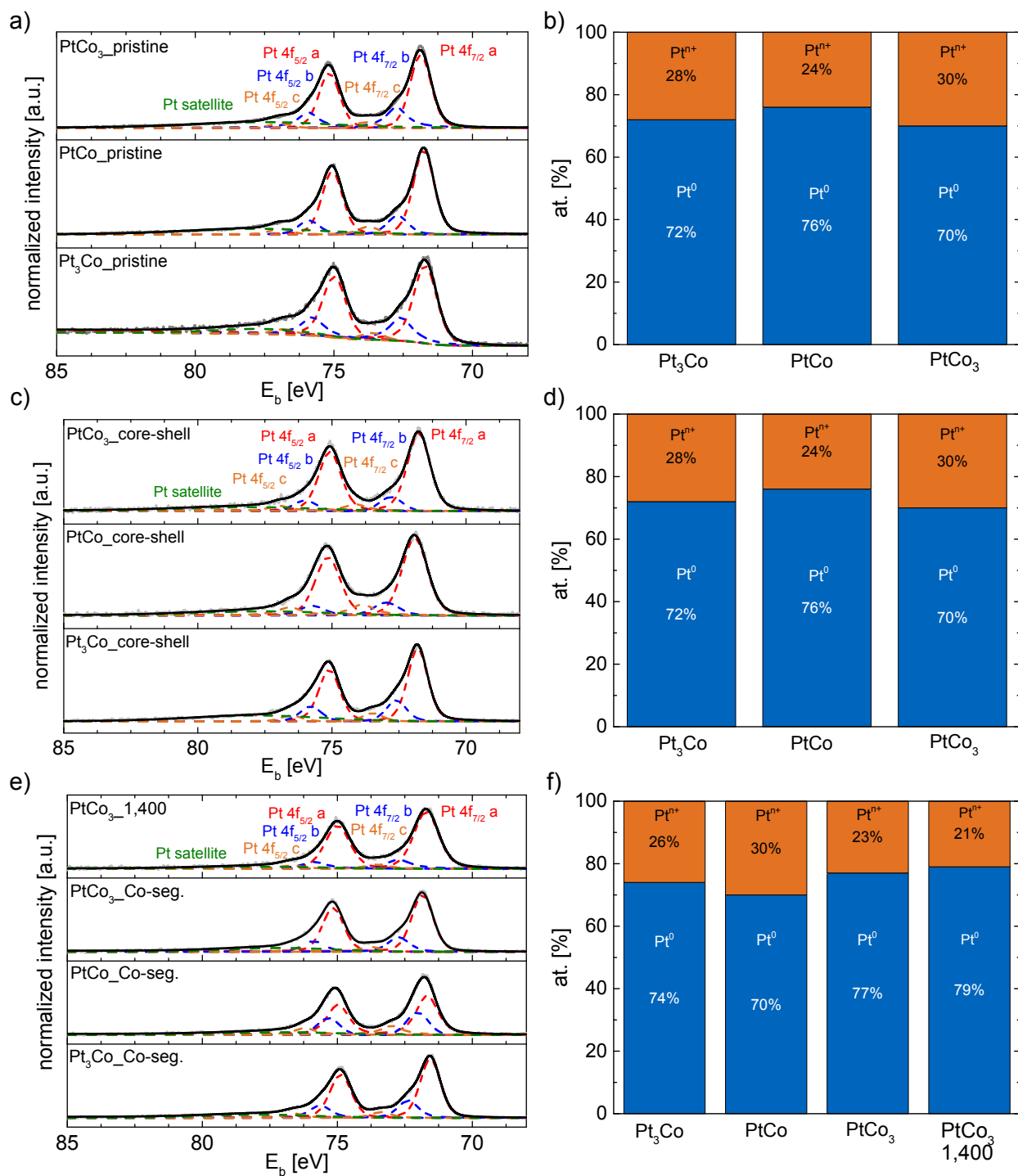


Figure S3. (a, c, e) High-resolution XPS spectra of Pt 4f for Pt₃Co, PtCo and PtCo₃ along the pristine alloy (a), dealloyed (c) and Co-segregated (e) core-shell nanoparticle motifs. Experimental parameters of the XPS measurements are listed in Table S2. The experimental data are denoted in grey, while the resulting envelope is symbolized in black. The different oxidation states of Pt species are denoted in red (Pt⁰), blue (Pt²⁺), and orange (Pt⁴⁺) dashed lines. (b, d, f) Bar diagrams display the atomic Pt⁰:Ptⁿ⁺ ratios for the pristine and treated Pt_xCo_{1-x} catalysts appearing in their various structural motifs.

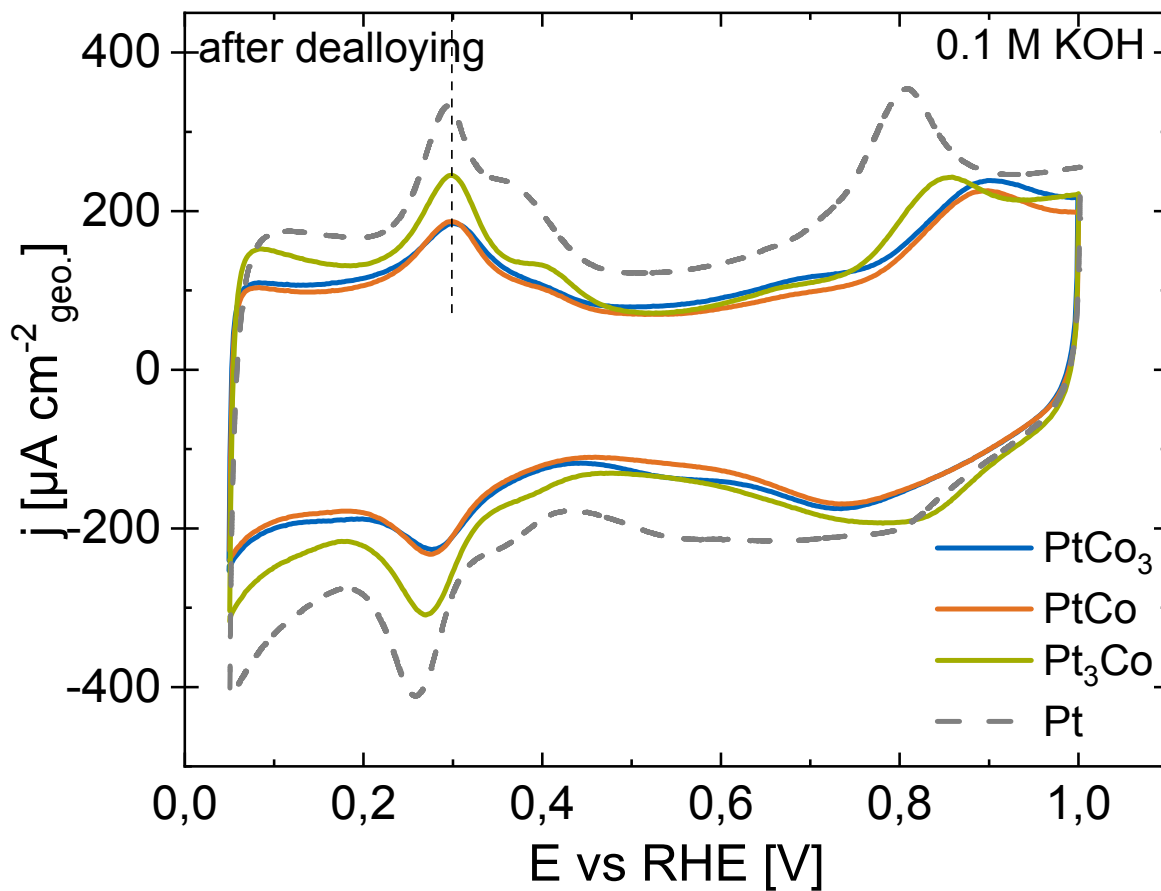


Figure S4. CV profiles of the dealloyed PtCo_3 (blue), PtCo (orange), and Pt_3Co (green) core-shell catalysts in Ar-saturated 0.1 M KOH recorded with a scan rate of 50 mV s^{-1} and a Pt loading $\sim 10 \mu\text{g}_{\text{Pt}} \text{ cm}_{\text{geo}}^{-2}$. The current density is normalized to the geometric area of the electrode. Pure Pt/HSAC (grey dashed line) was taken as reference. The vertical black dashed line denotes no alteration in the potential of current peak in the H desorption process.

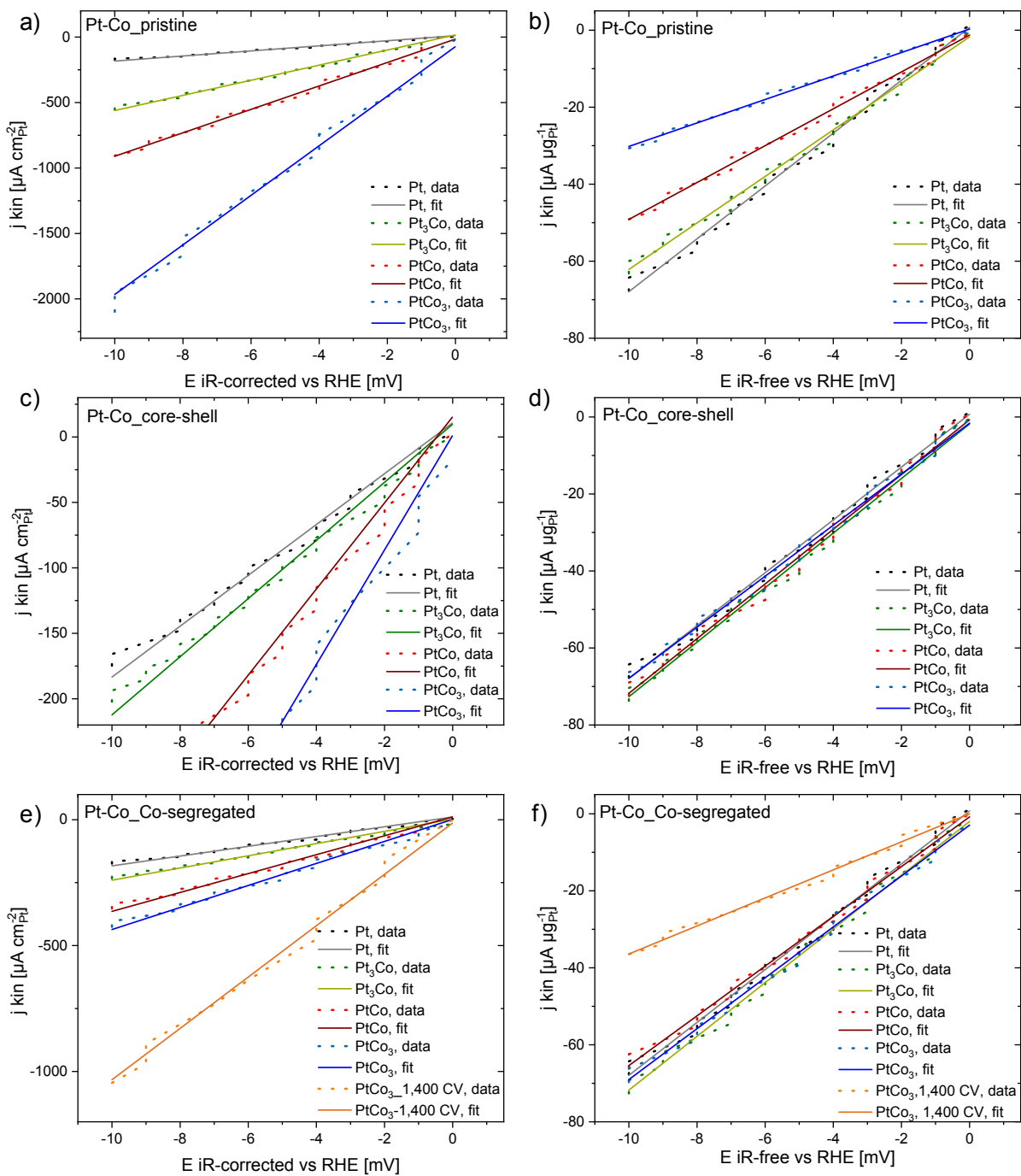


Figure S5. HER micro-polarization curves for Pt_xCo_{1-x} electrocatalysts in the pristine alloy (a, b), dealloyed Pt-rich shell (c, d) and Co-segregated (e, f) core-shell nanoparticle motifs.. Experimental data are denoted with points, while the thin solid lines show the corresponding fits based on the simple linearization of the B.V. equation. The current density is normalized to the measured electrochemically active Pt surface area (left) and to the Pt mass used (right).

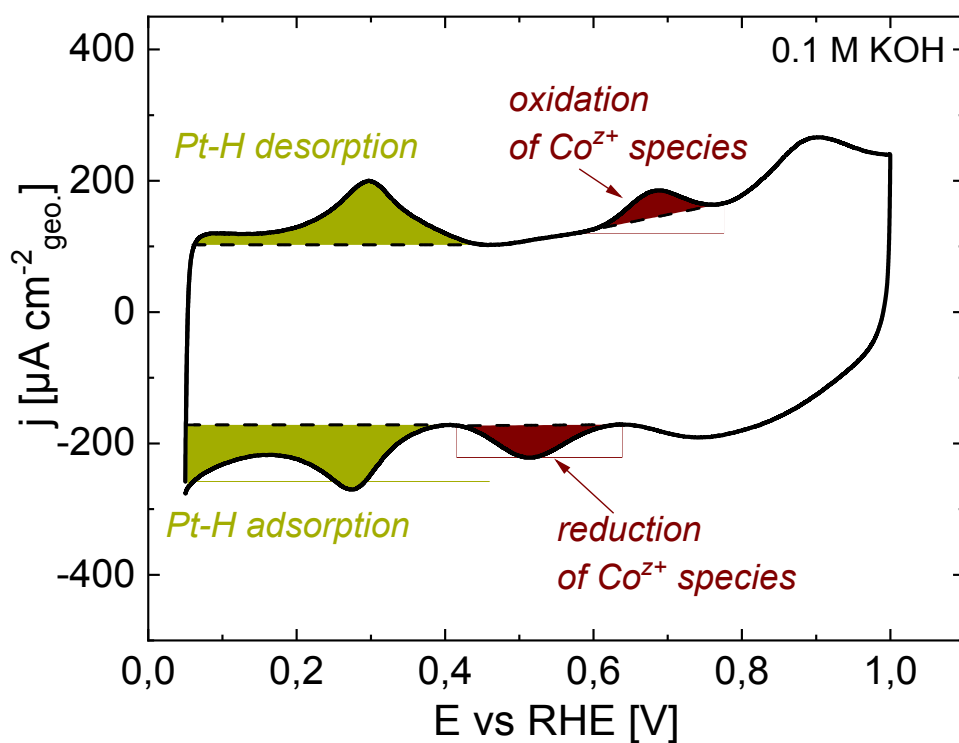


Figure S6. Illustration of the here developed descriptor to evaluate the elemental distribution of Pt and Co within the first surface layers and thus to point out the role of cobalt as an oxophilic component for the catalytic HOR performance in alkaline environment. The charges yielded from the hydrogen ad/desorption is divided by transferred charge for Co(hydr)oxide reduction/formation, so called $Q(\text{Hupd})/Q(\text{Co}^{z+})$ ratio. According to Pourbaix diagram, the transferred charge is assigned to the redox pair of $\text{Co}_3\text{O}_4/\text{Co}(\text{OH})_2$ by $3 \text{Co}(\text{OH})_2 + 2 \text{OH}^- \rightarrow \text{Co}_3\text{O}_4 + 4 \text{H}_2\text{O} + 2e^-$.

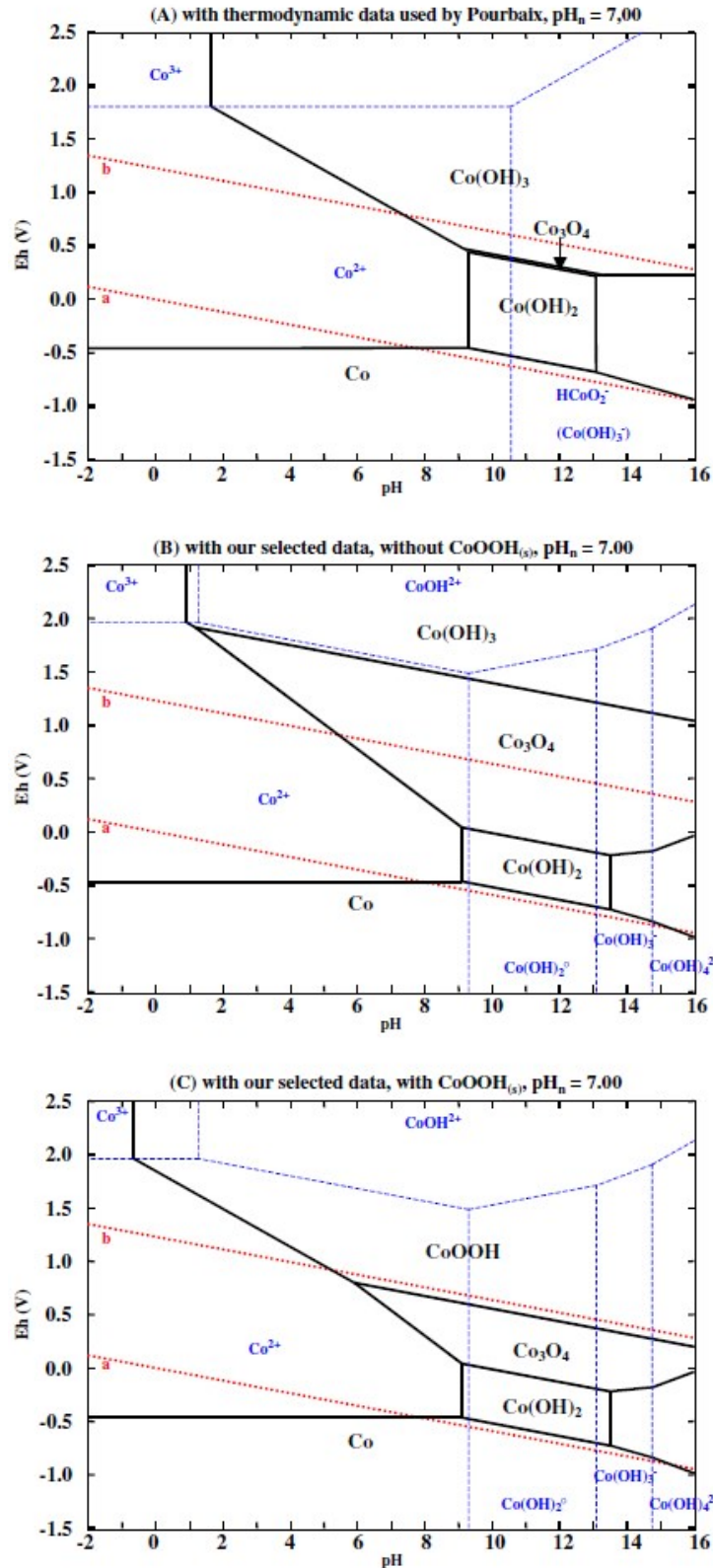


Figure S7. Pourbaix diagram of bulk phases (a) without and (b, c) corrected by experimental free energies of aqueous ions adopted from Chivot et al. The concentration of Co ions was constant at $10^{-6} \text{ mol kg}^{-1}$.

Chivot, J.; Mendoza, L.; Mansour, C.; Pauporté, T.; Cassir, M., New insight in the behaviour of Co–H₂O system at 25–150°C, based on revised Pourbaix diagrams. *Corrosion Science* 2008, 50 (1), 62–69.

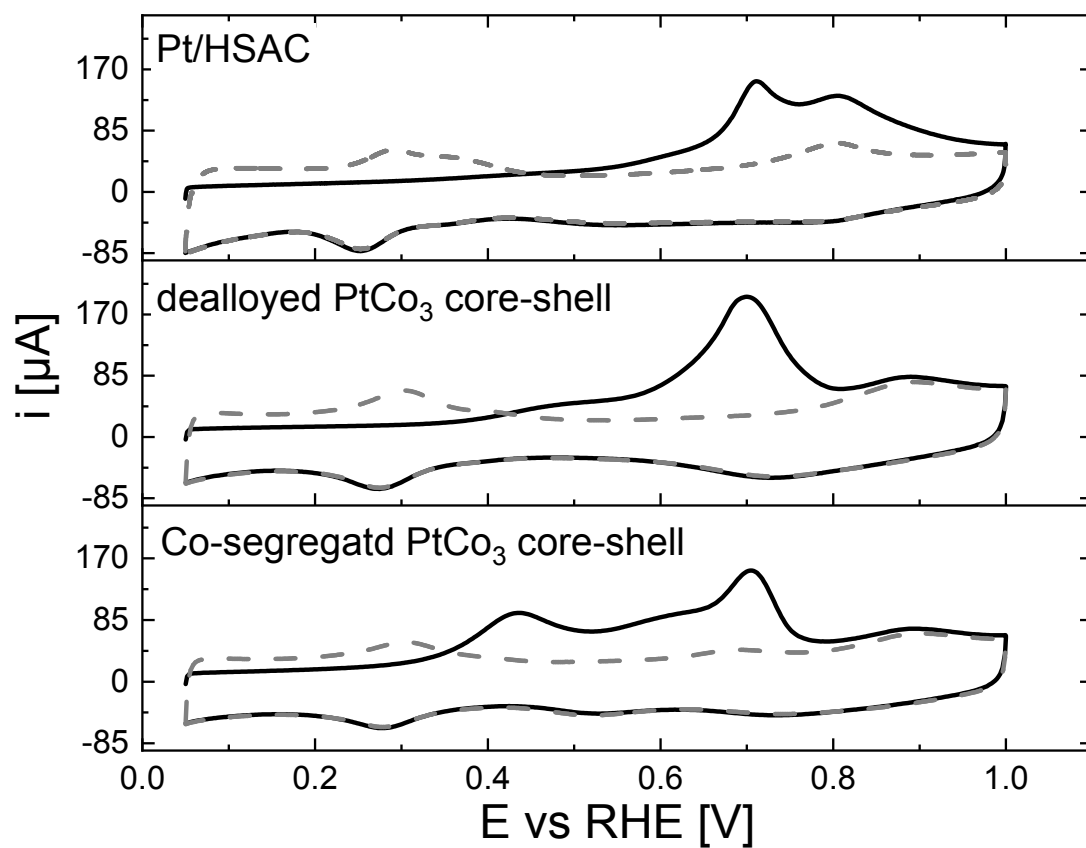


Figure S8. CO stripping profiles of Pt/HSAC (panel top), dealloyed (panel middle) and Co-segregated (panel bottom) PtCo₃ core-shell catalysts in 0.1 M KOH recorded with a scan rate of 10 mV s⁻¹ and a Pt loading ~ 10 μg_{Pt} cm_{geo}⁻². The grey dashed line illustrates the first CV profile after electrochemical oxidation of CO monolayer (black solid line).