

Electronic Supplementary Information

Niobium Oxide Coatings on Nanostructured Platinum Electrocatalysts: Benefits and Limitations

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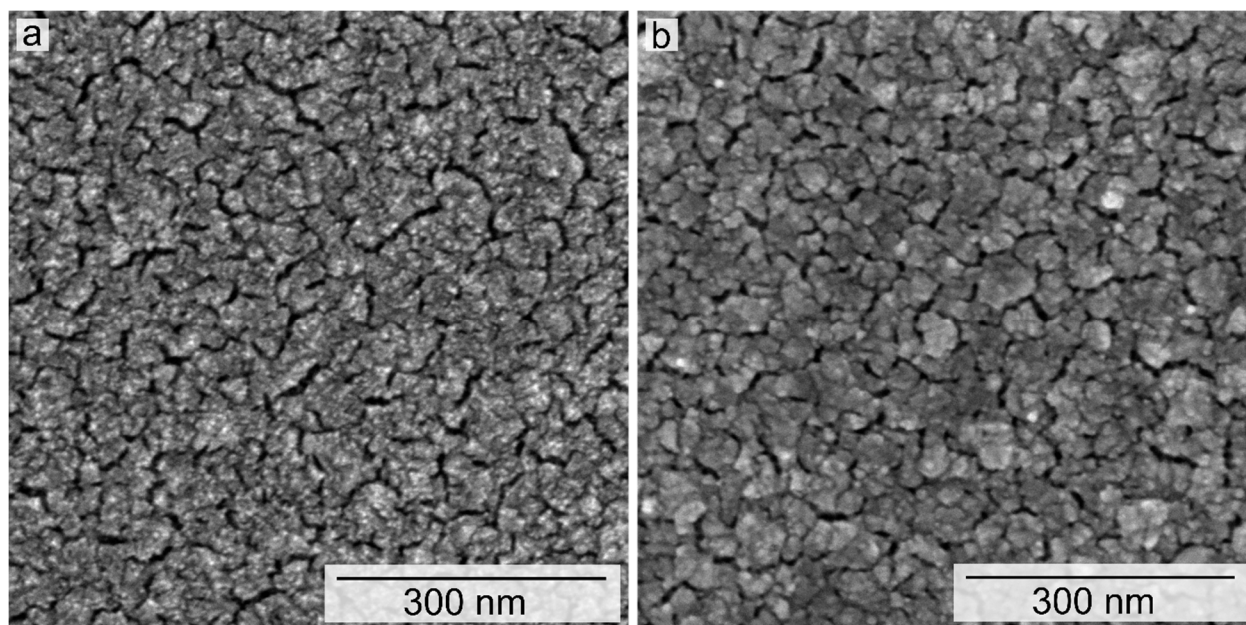


Figure S1. A series of scanning electron microscopy (SEM) images of electrodeposited films of nanotextured Pt with (a) 0.5 nm thick and (b) 4.5 nm thick layers of Nb₂O₅.

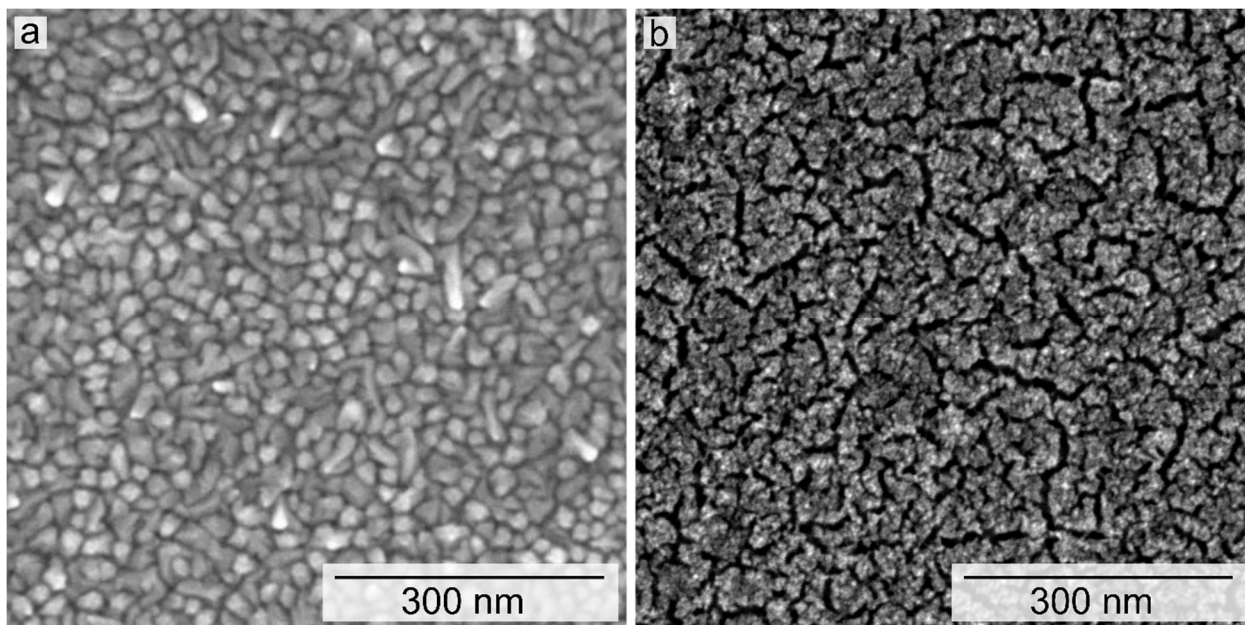


Figure S2. (a) Image of a polished Si wafer coated with a Pt film deposited by physical vapour deposition (PVD). (b) Image of an electrodeposited Pt film after heating for 3 h at 250 °C in the high vacuum atomic layer deposition chamber, but without introduction of the Nb-precursor.

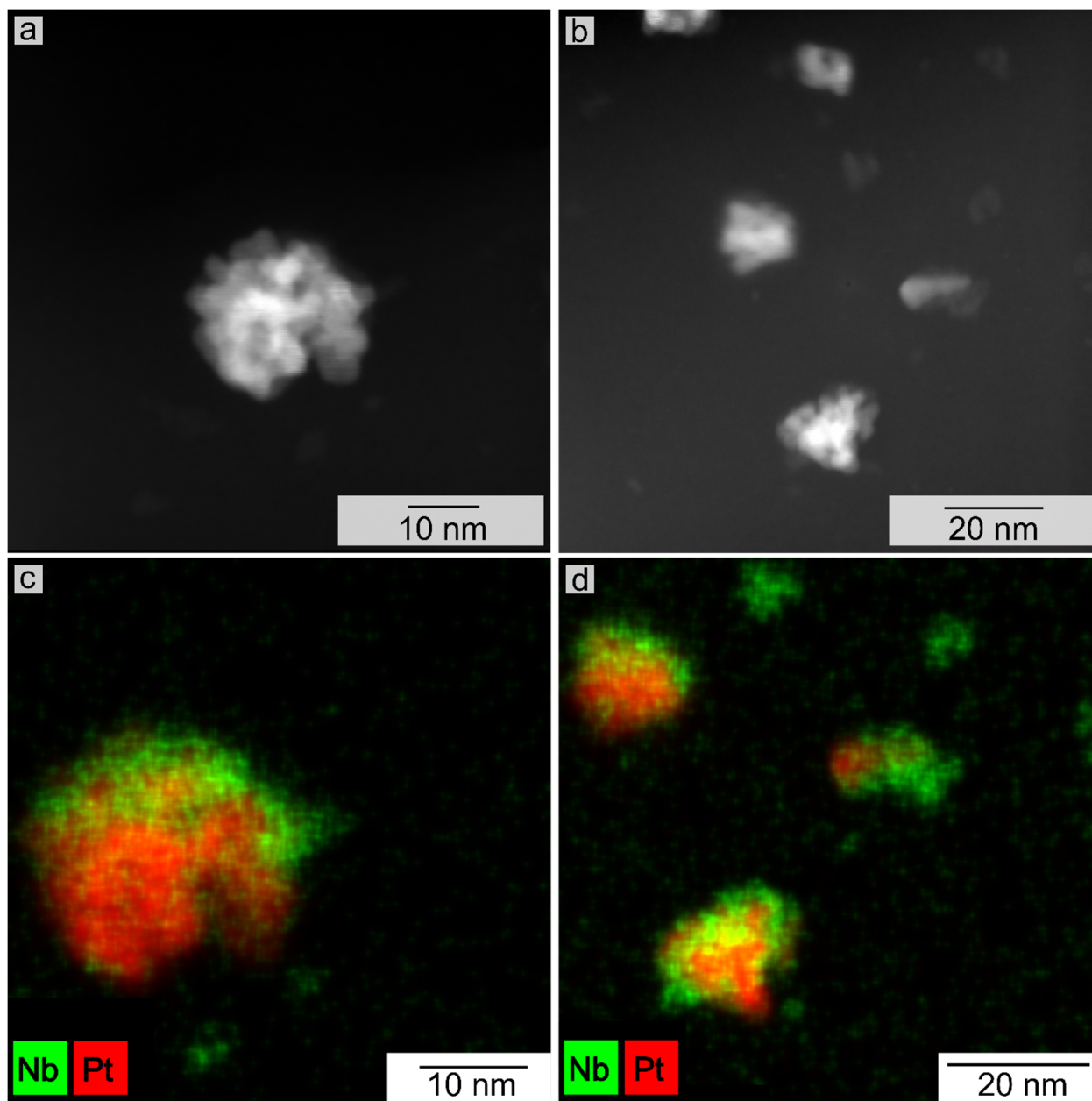


Figure S3. High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images of 3 nm thick layers of Nb₂O₅ coated on electrodeposited Pt (a,b) and the corresponding overlaid elemental maps for the Pt L α and Nb K α signals from the energy dispersive X-ray spectroscopy analyses (c,d). The samples for STEM and EDS analysis were prepared by gently scraping the electrodeposited Pt coated with Nb₂O₅ to detach it from the PVD Pt substrate. The detached particles were suspended in ethanol and deposited on a TEM grid for these analyses.

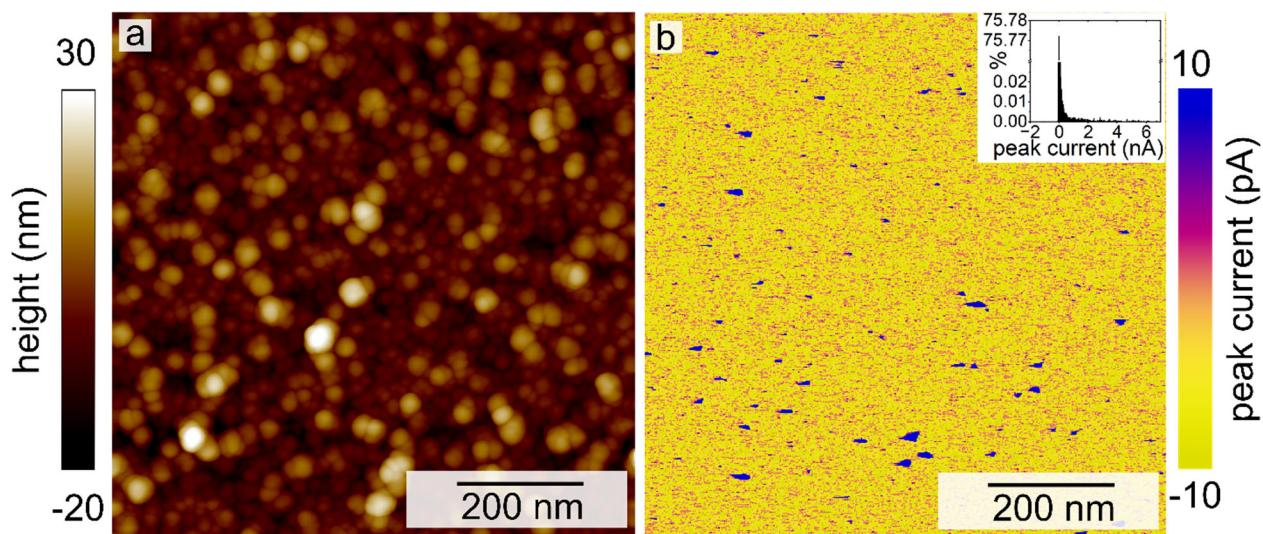


Figure S4. Conductive atomic force microscopy (C-AFM) images displaying (a) the measured sample height and (b) peak current for an electrodeposited Pt catalyst coated with a 3 nm thick layer of Nb₂O₅. The peak current values were limited to ± 10 pA to better visualize the relative electrical conductivity across the surfaces of the electrode.

Table S1. Comparison of observed Nb 3d, O 1s, and Pt 4f binding energies measured by X-ray photoelectron spectroscopy for samples prepared in this work to values reported in the literature.

sample	Binding energy (eV)					reference
	Nb 3d _{5/2}	Nb 3d _{3/2}	O 1s (lattice)	Pt 4f _{7/2}	Pt 4f _{5/2}	
Nb metal	202.2	204.9	-	-	-	(1)
NbO	204.4	207.1	531.0	-	-	(1)
NbO ₂	206.1	208.8	529.7	-	-	(2)
Nb ₂ O ₅	207.7	210.4	531.7	-	-	(3)
Pt metal	-	-	-	71.2	74.5	(4)
PtO ₂	-	-	530.3	74.1	77.4	(4)
0 nm Nb ₂ O ₅	-	-	530.2	70.8	74.1	this work
0.5 nm Nb ₂ O ₅	207.7	210.4	530.7	70.4	73.8	this work
3 nm Nb ₂ O ₅	207.6	210.3	530.5	70.9	74.3	this work
4.5 nm Nb ₂ O ₅	207.6	210.3	530.6	70.8	74.1	this work
0 nm Nb ₂ O ₅ after AST	-	-	535.2	71.3	74.1	this work
3 nm Nb ₂ O ₅ after AST	207.8	210.6	531.7	71.0	74.3	this work

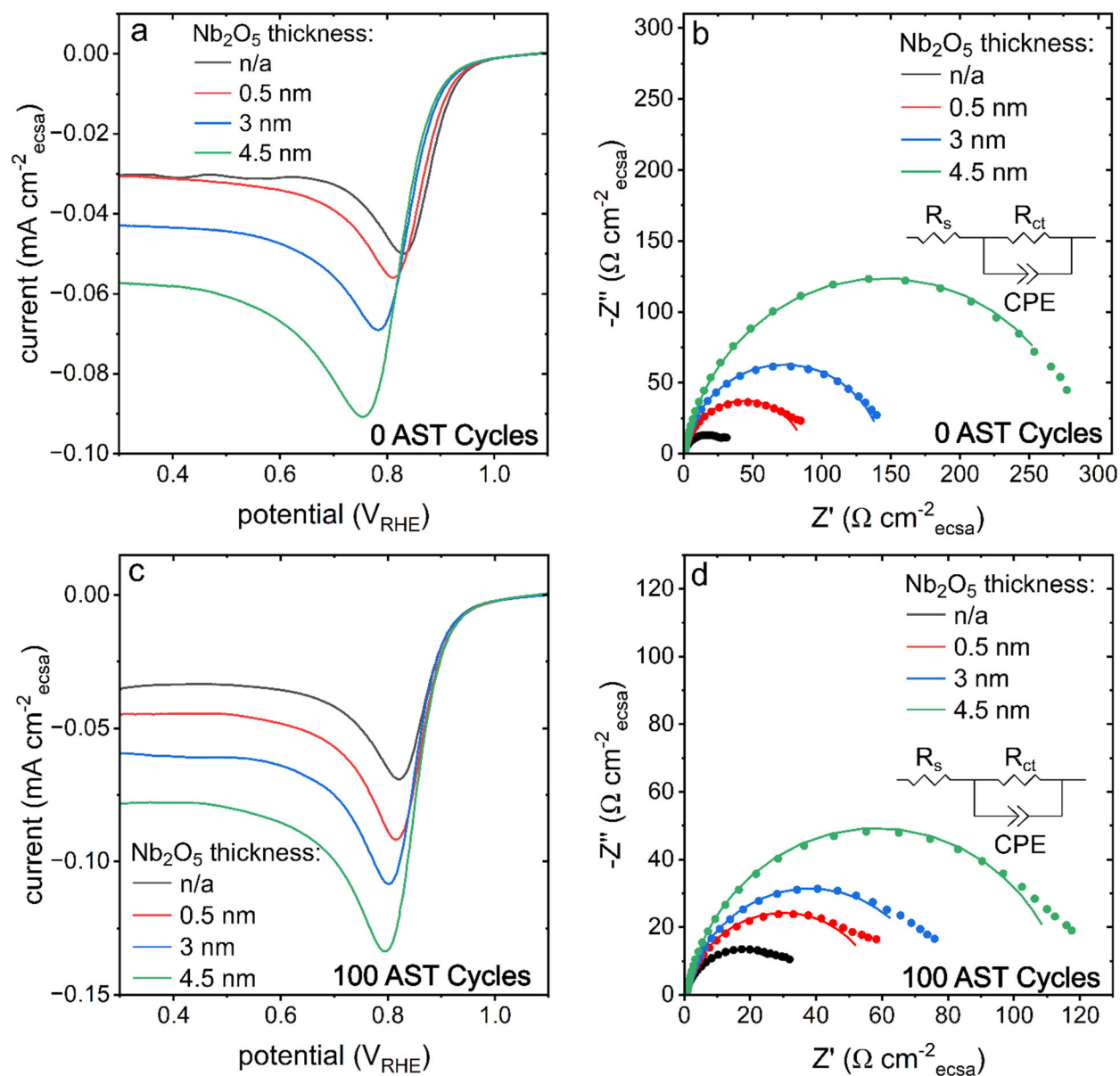


Figure S5. Linear sweep voltammetry plots recorded at a scan rate of 10 mV/s in an O₂ (g) saturated electrolyte for the nanostructured Pt and niobia coated nanostructured Pt both (a) before and (c) after performing 100 AST cycles. A series of Nyquist plots were recorded at 0.9 V_{RHE} in an O₂ saturated electrolyte for the same samples both (b) before and (d) after the 100 cycles of the AST, wherein the fits (solid lines) correspond to the circuits displayed in the insets.

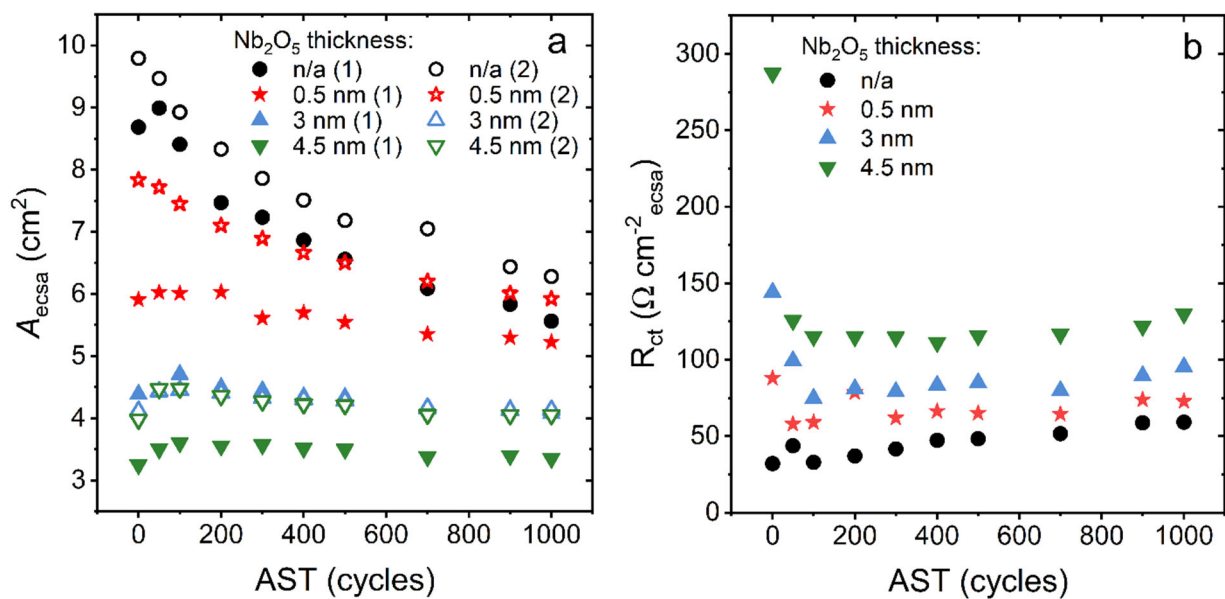


Figure S6. (a) Electrochemically active surface area (A_{eCSA}) and (b) charge transfer resistance (R_{ct}) of the pristine nanostructured Pt (black, squares), and the nanostructured Pt coated with 0.5 nm (red, circles), 3 nm (blue, triangles), and 4.5 nm (green, inverted triangles) thick layers of Nb_2O_5 . These properties were measured over the course of 1000 cycles of an accelerated stress test.

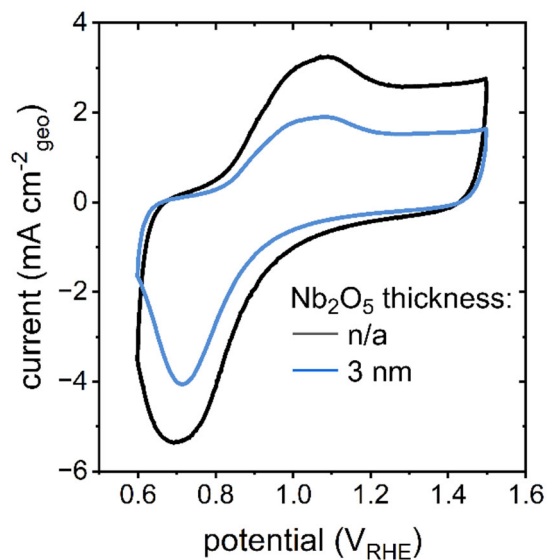


Figure S7. Representative cyclic voltammetry (CV) plots of the 100th AST cycle applied to a pristine, uncoated Pt catalyst and a Pt catalyst coated with a 3 nm thick layer of Nb₂O₅. The analysis was conducted in N₂ (g) saturated 0.5 M H₂SO₄ at a scan rate of 500 mV/s. The upper and lower limits of the CV were 1.5 V_{RHE} and 0.6 V_{RHE}, respectively.

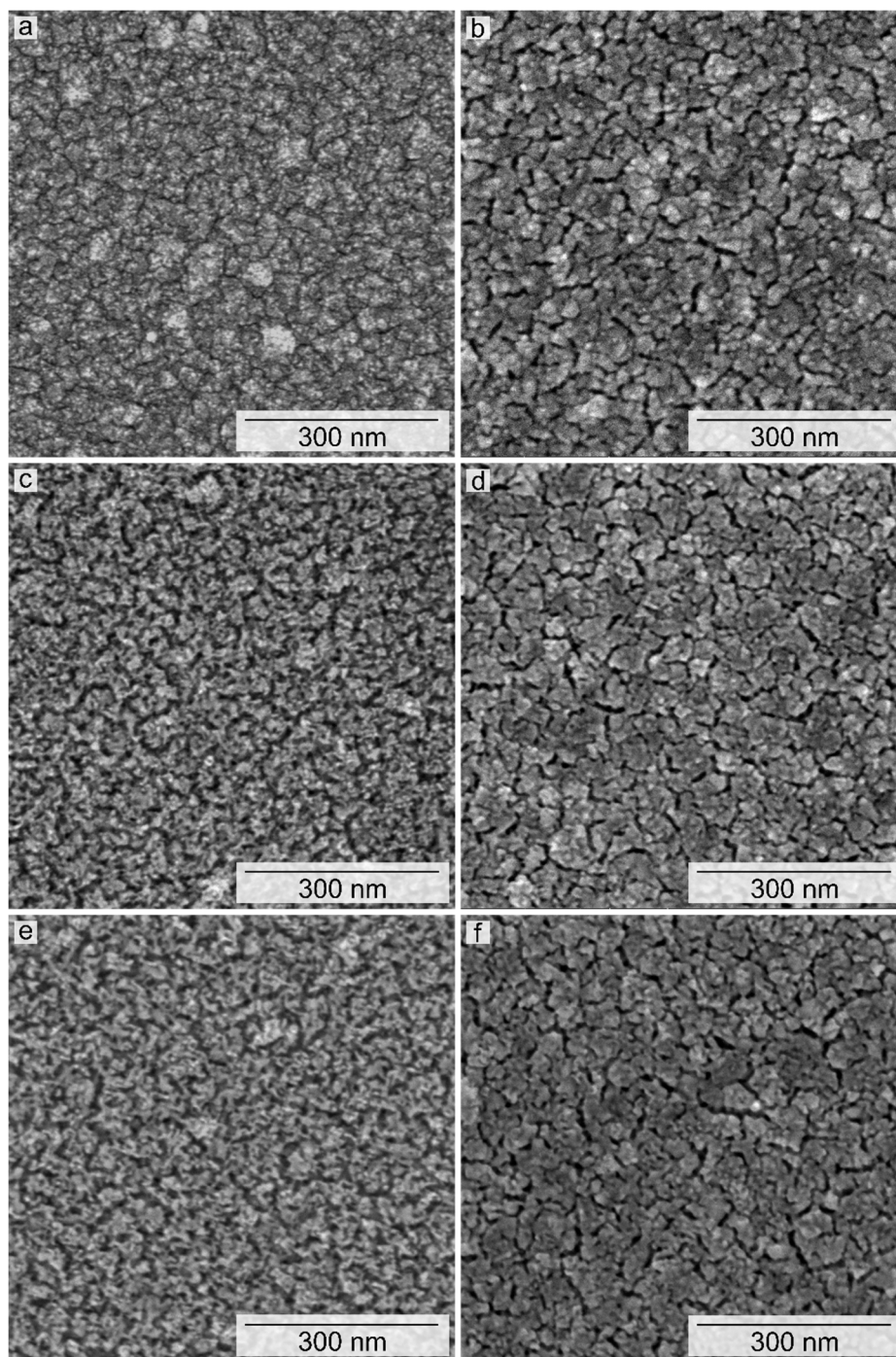


Figure S8. A series of scanning electron microscopy (SEM) images of pristine Pt with a nanoscale texture (left) and the same substrate after coating with 3 nm thick layer of Nb₂O₅ (right). These images were taken either (a,b) before electrochemical cycling, (c,d) after 500 cycles of an AST, or (e,f) after 1000 cycles of an AST.

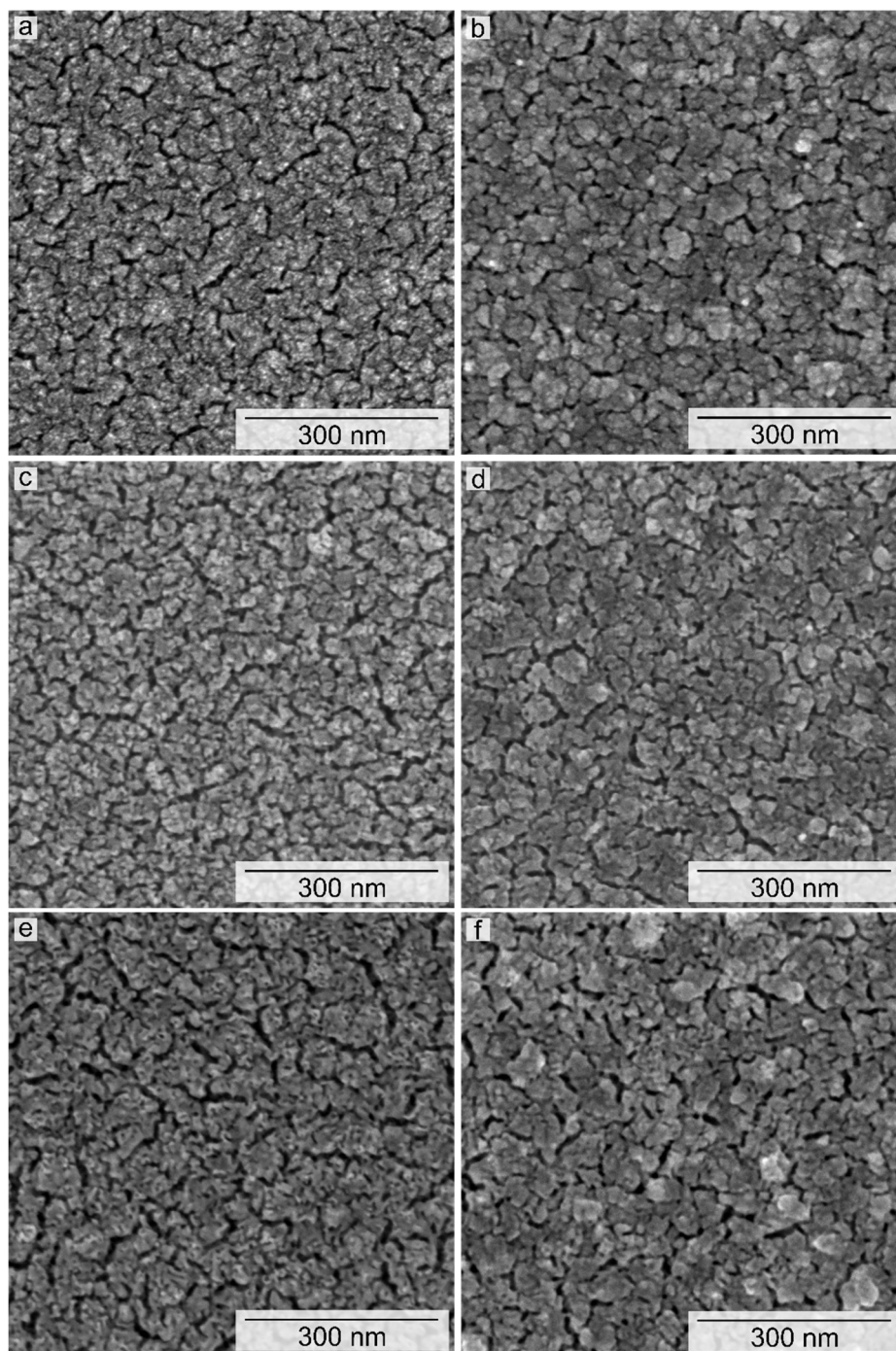


Figure S9. A series of scanning electron microscopy (SEM) images of 0.5 nm thick (left) and 4.5 nm thick (right) layers of Nb₂O₅ that coat the electrodeposited films of nanotextured Pt. These SEM images were obtained (a,b) before electrochemical cycling, (c,d) after 500 cycles of an accelerated stress test (AST), and (e,f) after 1000 cycles of an AST.

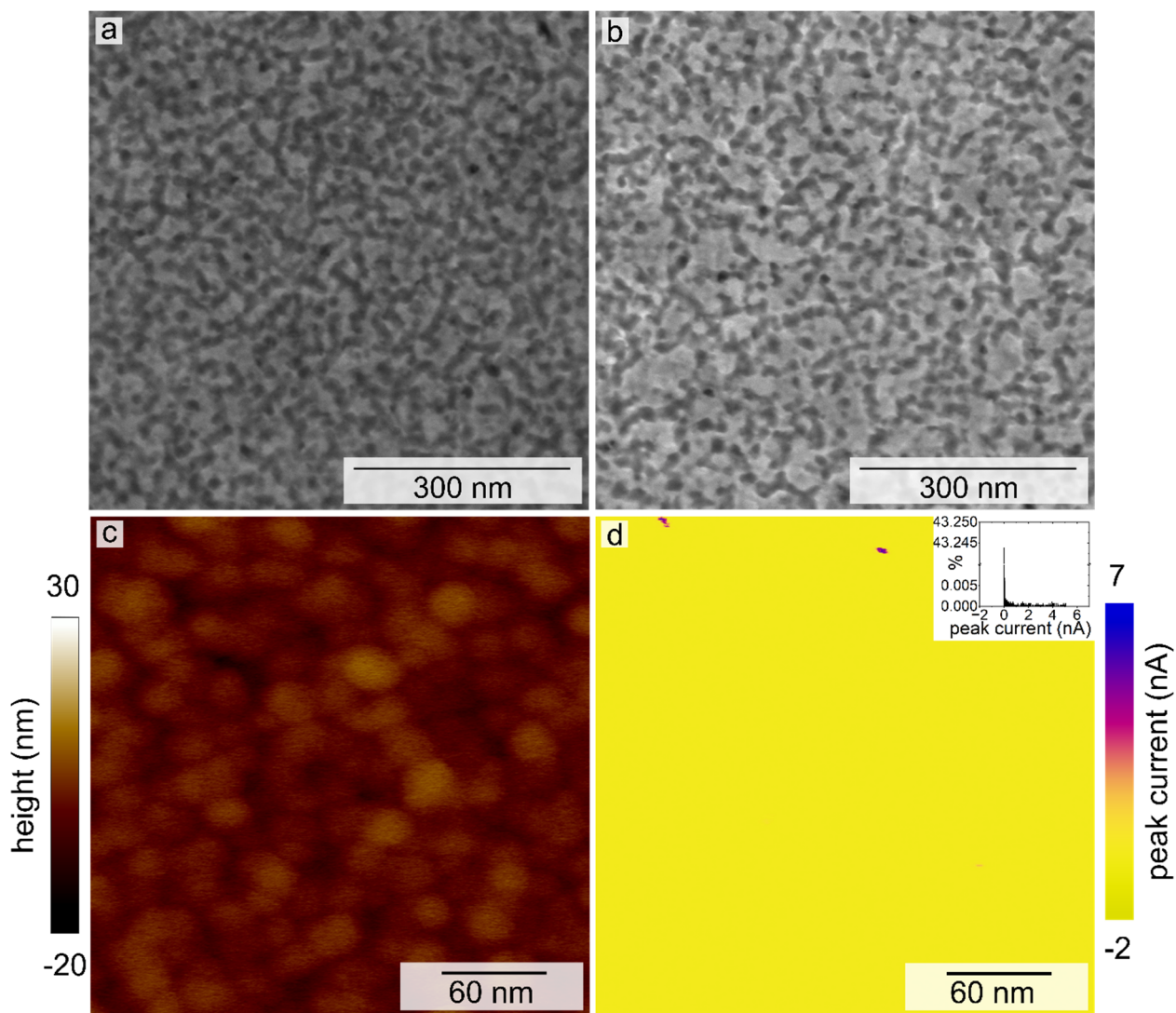


Figure S10. Scanning electron microscopy (SEM) images of nanostructured Pt coated with (a) 3 nm thick and (b) 4.5 nm thick layers of Nb₂O₅. Conductive atomic force microscopy (C-AFM) images displaying the measured (c) sample height and (d) peak current for an electrodeposited Pt catalyst coated with a 3 nm thick layer of Nb₂O₅. These images were obtained after 5,000 cycles of an AST.

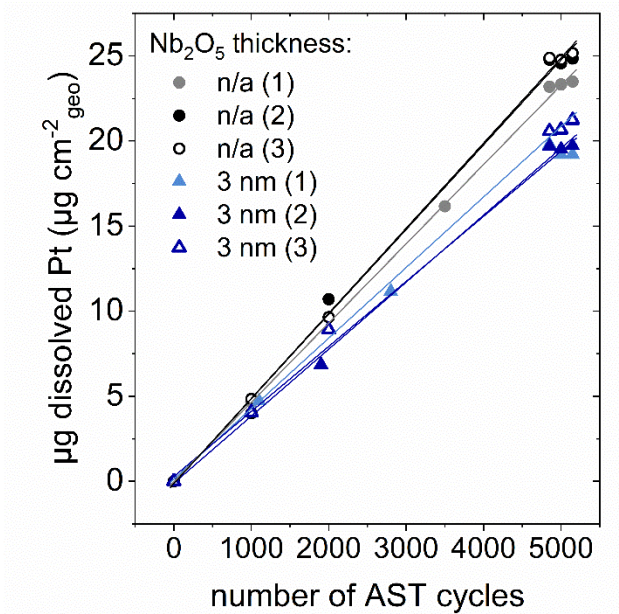


Figure S11. Mass of Pt dissolved into the electrolyte as a function of the number of AST cycles performed by electrochemical techniques for both the pristine nanostructured Pt (circles, grey-scale) and the same nanostructured Pt with a 3 nm thick coating of Nb₂O₅ (triangles, blue). Separate measurements were obtained at certain time points in the AST for three separate samples of each type of sample (e.g., pristine Pt or nioba coated Pt). Three separate measurements at 5,000 AST cycles from three different samples of each sample type were each offset horizontally for clarity.

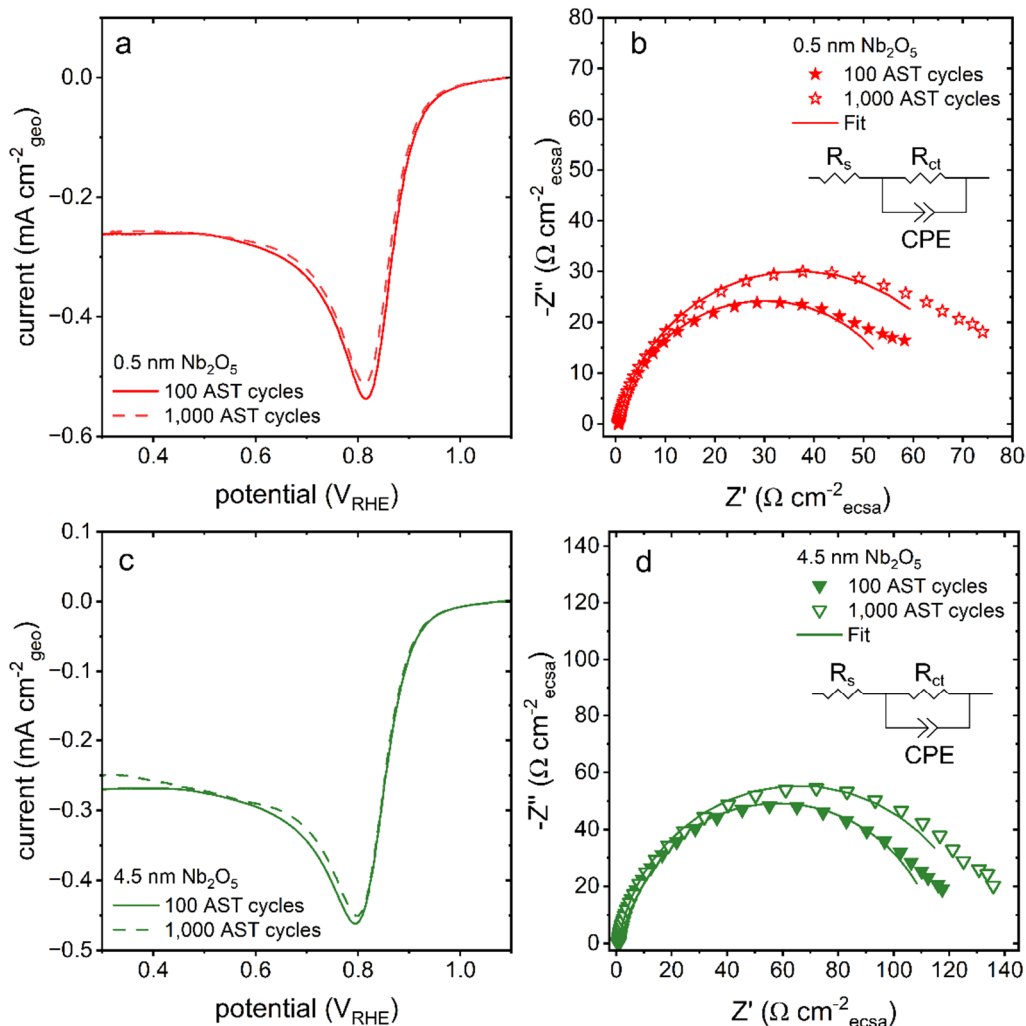


Figure S12. (a,c) Linear sweep voltammetry plots recorded at a scan rate of 10 mV/s in an O₂ (g) saturated electrolyte for niobia coated nanostructured Pt samples after performing (solid line) 100 cycles and (dashed line) 1,000 cycles of the AST. (b,d) Nyquist plots recorded at 0.9 V_{RHE} in an O₂ saturated electrolyte with fits (solid lines) corresponding to the circuits displayed in the insets also obtained after performing (solid symbols) 100 cycles and (hollow symbols) 1,000 cycles of the AST. The colours of the traces indicate the thickness of the Nb₂O₅ films where red corresponds to an 0.5 nm thick Nb₂O₅ and green to 4.5 nm thick Nb₂O₅.

References

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