Supplementary Information

Fine-Tuning the Surface Coverage of Niobium Oxide on Platinum Catalysts and Its Impact on the Oxygen Reduction Reaction

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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.

	binding energy (eV)							
sample	Nb $3d_{5/2}$	Nb $3d_{3/2}$	O 1s (lattice)	O 1s (–OH)	O 1s (H_2O)	Pt $4f_{7/2}$	Pt $4f_{5/2}$	ref.
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_2O_5	207.7	210.4	531.7	-	-	-	-	(3)
Pt metal	-	-	-	-	-	71.2	74.5	(4)
PtO_2	-	-	530.3	-	-	74.1	77.4	(4)
Pt EOT	-	-	-	532.1	533.3	71.2	74.6	this work
Pt-Nb_2O_5 BOT	207.6	210.4	531.1	532.9	534.8	-	-	this work
Pt-Nb_2O_5 EOT	207.6	210.2	530.8	532.6	534.0	71.5	74.9	this work

Table S2. Average advancing and receding water contact angles for each type of custom-prepared Pt-based electrocatalyst.

sample type	exposed Pt surface area (%)	θ_A (°)	θ_R (°)
Pt	100	63 ± 2	19 ± 2
Nb_2O_5 islands on Pt	~65	72 ± 4	48 ± 2
holes in Nb_2O_5 on Pt	~30	70 ± 4	38 ± 3

* Abbreviations: θ_A: Advancing water contact angle, θ_R: Receding water contact angle.

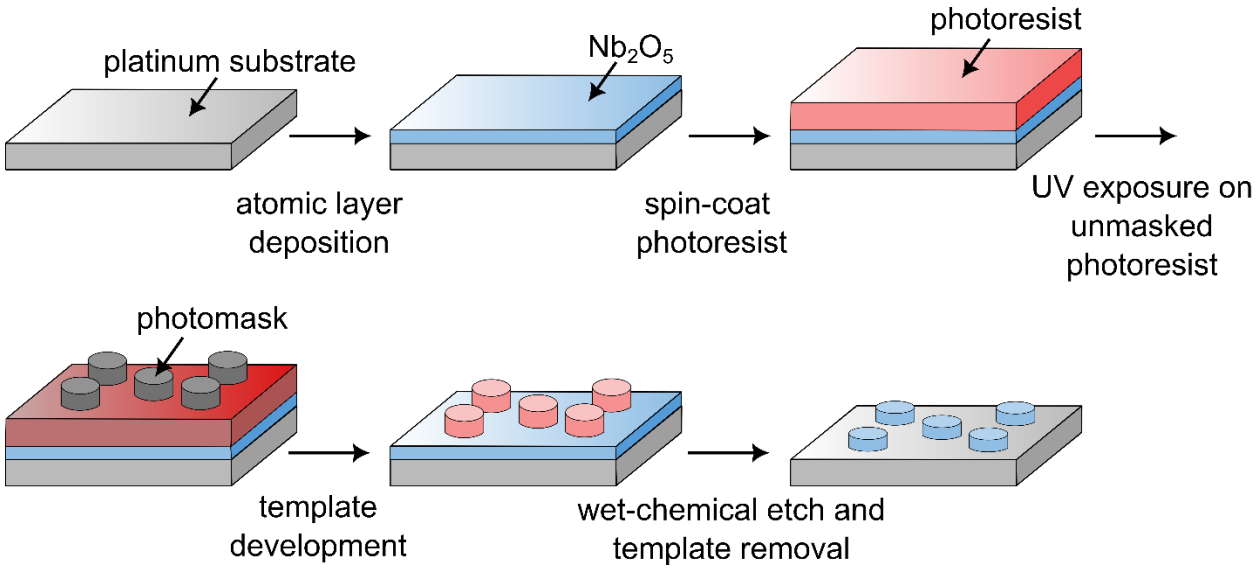

Figure S1. Schematic of the preparation of patterned niobium oxide (Nb_2O_5) films on platinum substrates. This example demonstrates the steps and patterns used to prepare arrays of circular niobium oxide islands supported on a platinum substrate.

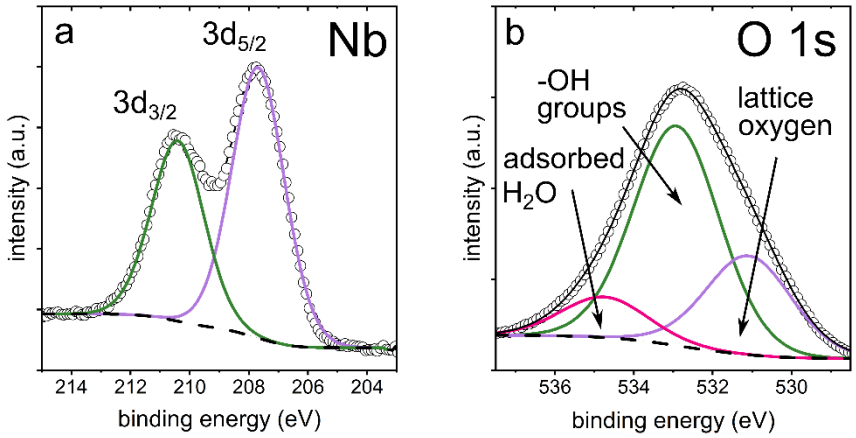

Figure S2. High resolution X-ray photoelectron spectroscopy (XPS) analyses of the (a) Nb 3d and (b) O 1s species present in the platinum catalyst coated with an ~1-nm thick Nb_2O_5 layer before electrochemical testing (BOT).

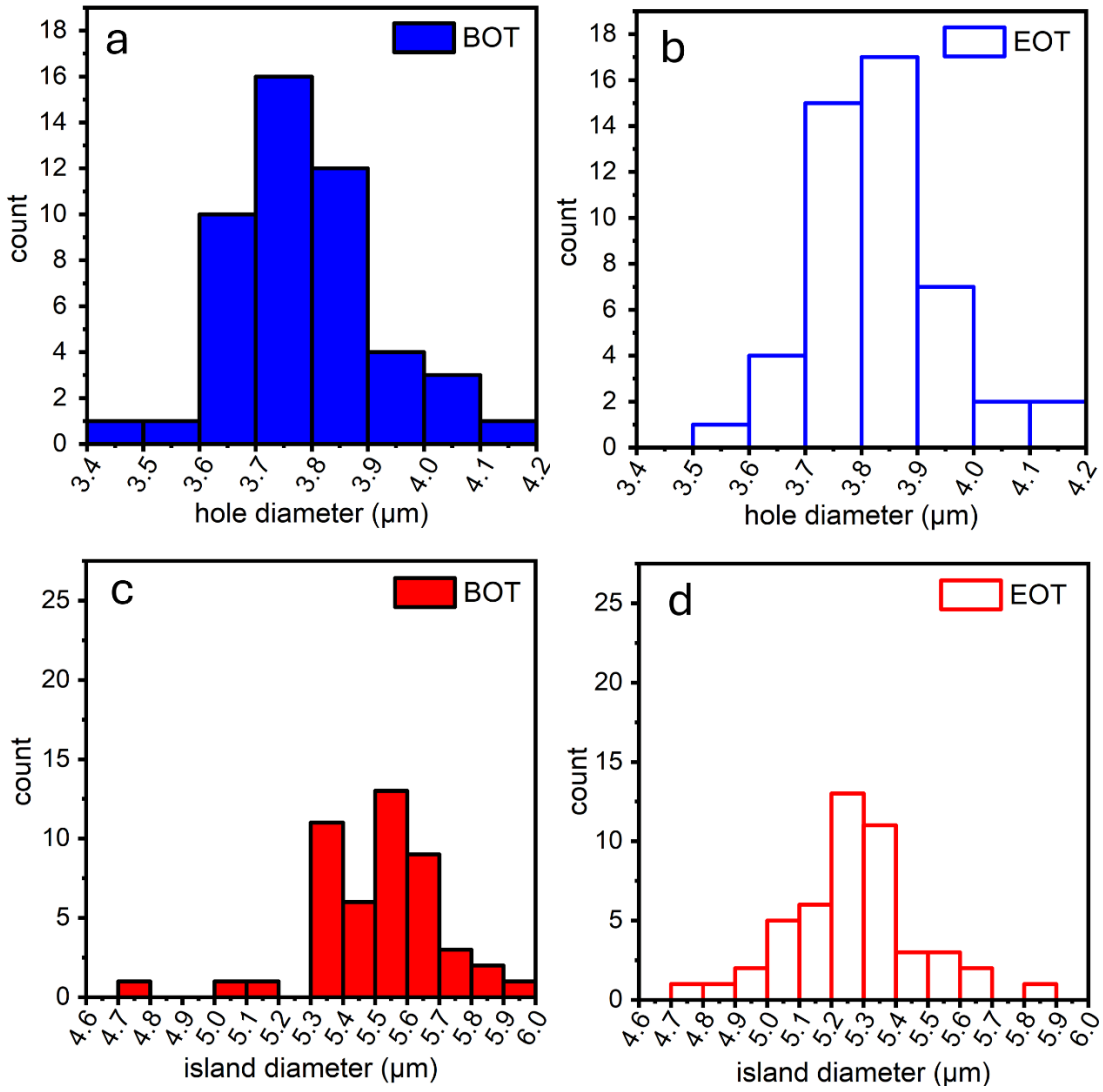

Figure S3. Diameter of the (a,b) circular holes and (c,d) circular islands of niobium oxide as measured from a series of scanning electron microscopy (SEM) images obtained (a,c) before and (b,d) after performing a durability test [i.e., 5,000 cycles of the applied potential from 0 to 1.3 V (vs. RHE) while immersing the electrodes in a sulfuric acid electrolyte].

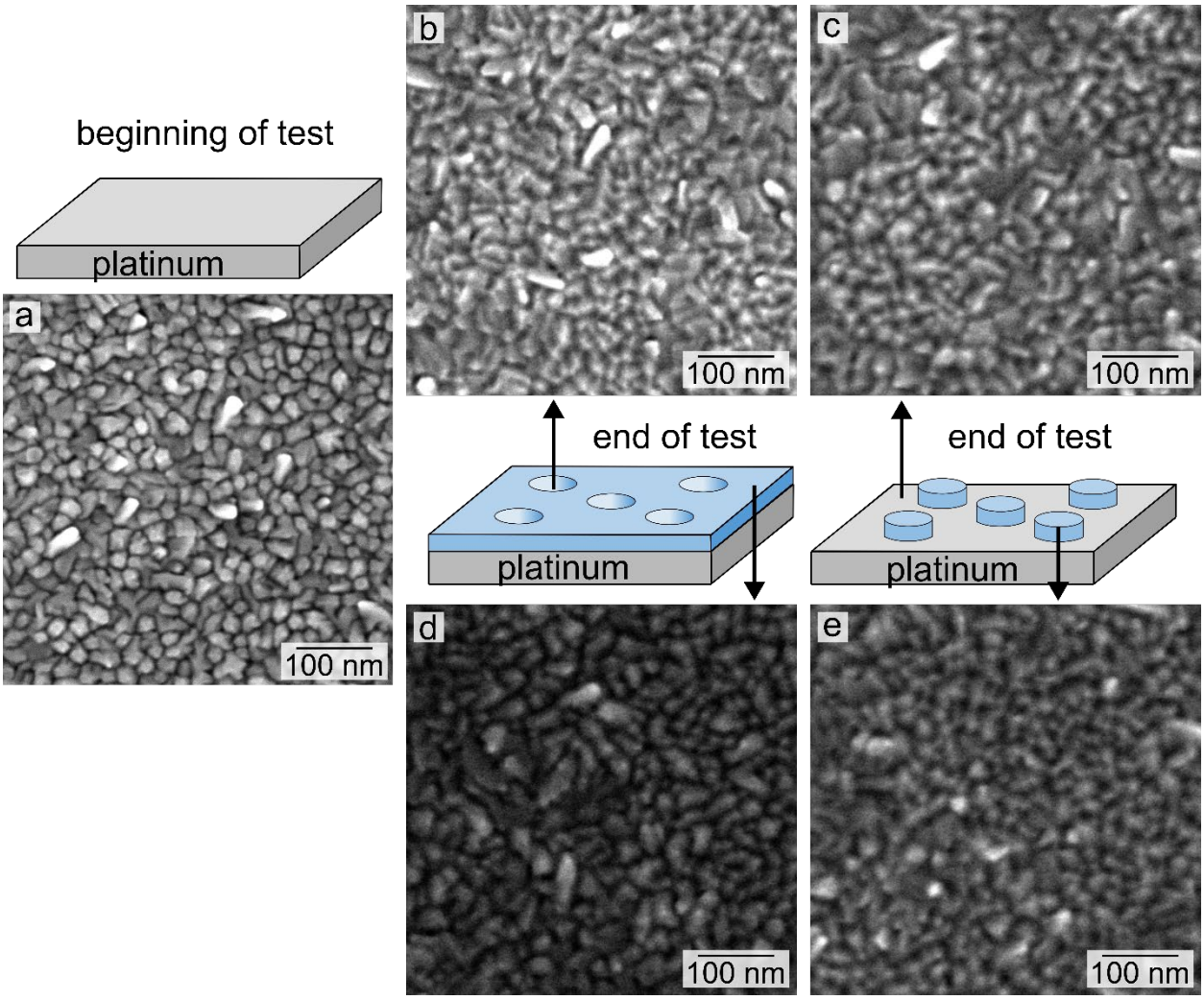

Figure S4. Representative SEM images of pristine, uncoated Pt electrocatalysts and two types of Pt electrocatalysts coated with ultrathin, patterned films of Nb_2O_5 with complementary features [e.g., (b,d) hexagonal arrays of circular holes in the niobium oxide film, or (c,e) hexagonal arrays of circular islands of niobium oxide]. The SEM images were obtained (a) before and (b–e) after a durability test (i.e., 5,000 cycles of the applied potential from 0 to 1.3 V (vs RHE) while immersing the electrodes in a sulfuric acid electrolyte).

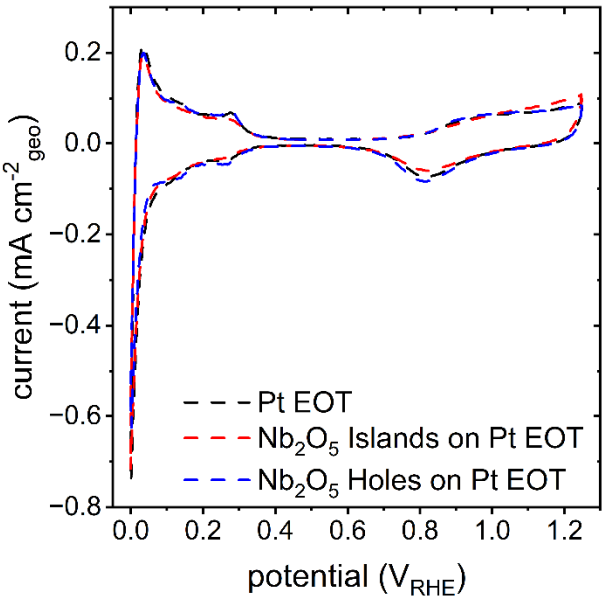

Figure S5. A series of cyclic voltammetry plots corresponding to the Pt catalysts (both without and with patterned coatings of Nb_2O_5 as indicated in the legend) after 5,000 cycles of a durability test (EOT).

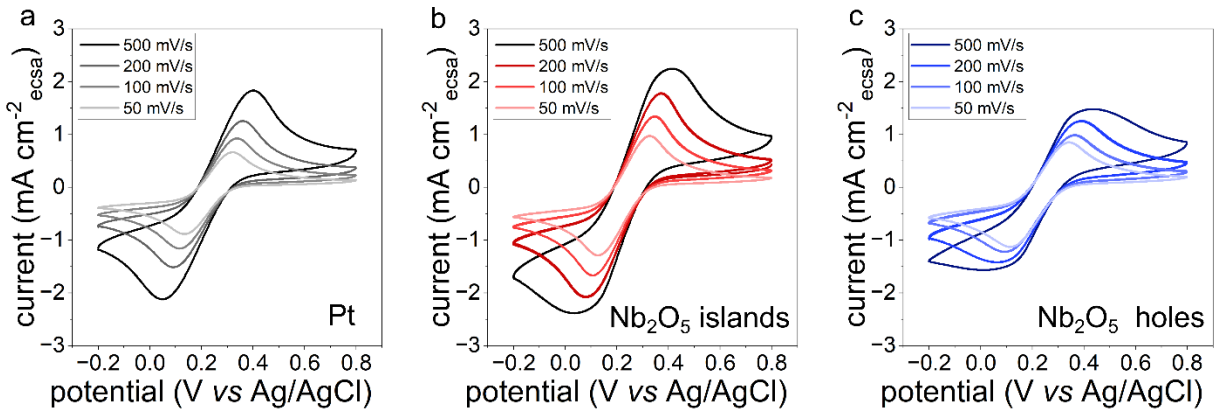

Figure S6. Cyclic voltammetry of potassium ferricyanide corresponding to (a) pristine Pt catalysts and arrays of (b)circular islands or (c) circular holes in a Nb_2O_5 film on Pt.

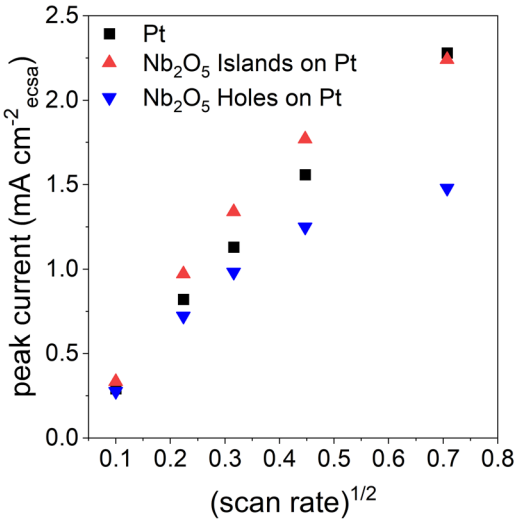

Figure S7. Relationship between the peak current of the potassium ferricyanide cyclic voltammetry plot and the square root of the scan rate for the pristine Pt and Pt coated with patterned niobium oxide.

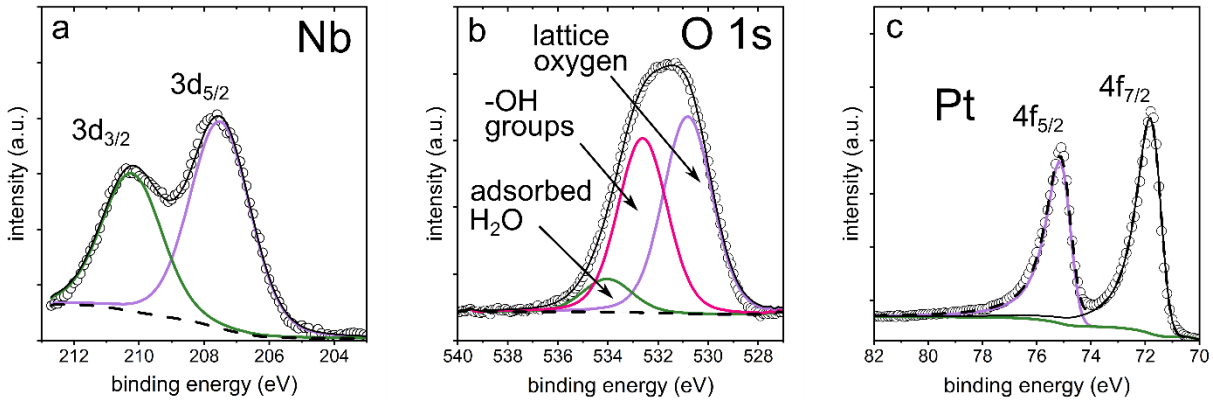

Figure S8. High resolution XPS analyses of the (a) Nb 3d, (b) O 1s, and (c) Pt 4f species present in the platinum catalyst coated with an ~1-nm thick Nb_2O_5 layer after being subjected to durability testing (EOT).

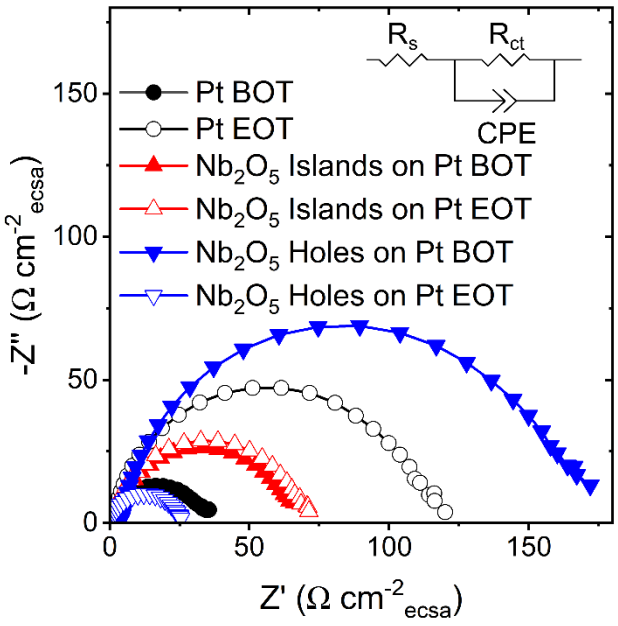

Figure S9. Nyquist plots normalized to the A_{ecsa} recorded at 0.9 V_{RHE} in O_2 saturated electrolyte at BOT (solid symbols) and EOT (hollow symbols) with fits (solid lines) corresponding to the inset circuit.

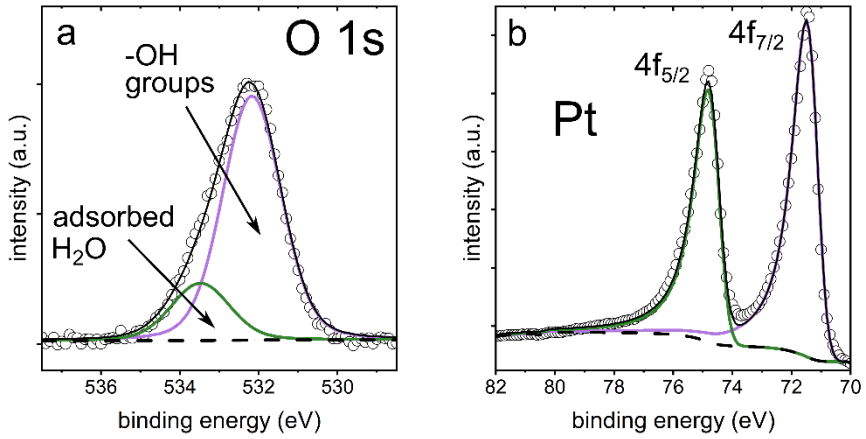

Figure S10. High resolution XPS analyses of the (a) O 1s and (b) Pt 4f species present in the pristine platinum catalyst after being subjected to durability testing (EOT).

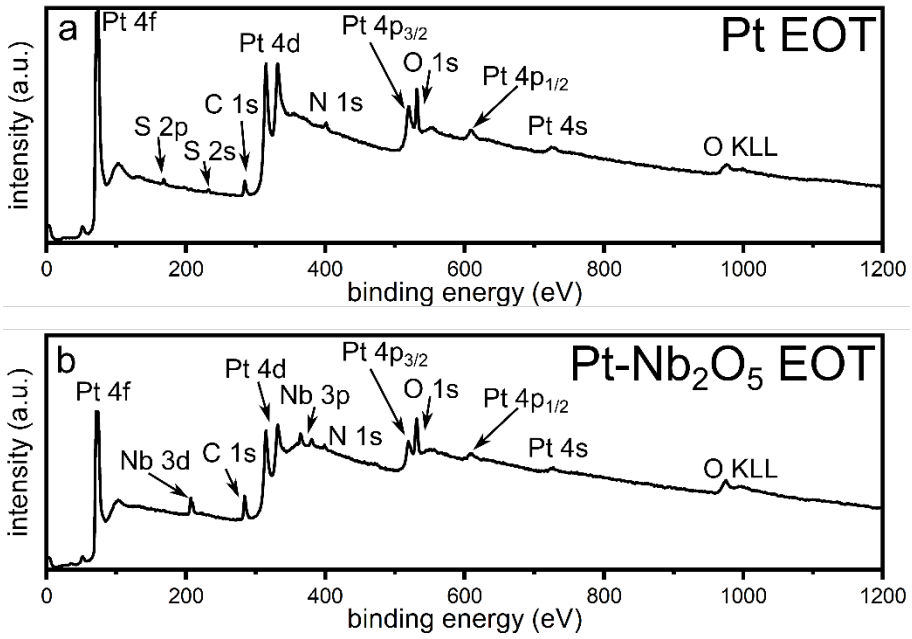

Figure S11. X-ray photoelectron spectroscopy survey spectra of the (a) pristine Pt catalyst and (b) Pt catalyst coated with ~1-nm thick Nb_2O_5 after being subjected to durability testing (EOT).

References

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