Supporting information

Porous Alumina Protective Coatings on Palladium Nanoparticles by Self-Poisoned Atomic Layer Deposition

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Table S1. Binding energies (BE) of selected surface intermediates (in eV) in their most stable configurations.

Intermediates	BE on Pd(111)	BE on Pd(211)
H[a]	0.58	0.52
CH_3	1.88	2.03
OH	2.61	3.18
$Al(CH_3)_3$	1.36	--
$Al(CH_3)_2$	3.47	3.66
$AlCH_3$	4.14	4.65
AlOH	3.42	3.96
$Al(OH)_2$	3.31	3.66
$Al(OH)_3$	1.14	1.51

$BE_M = E_M - E_{surf} - E_{M(g)}$. [a]$BE_H$ is calculated relative to the gas phase H_2 and clean surface. BE_M is the BE of surface intermediate; E_M is the total energy of surface intermediate; E_{surf} is the total energy of clean surface (either Pd(111) or Pd(211)); and $E_M(g)$ is the total energy of surface intermediate in gas phase.

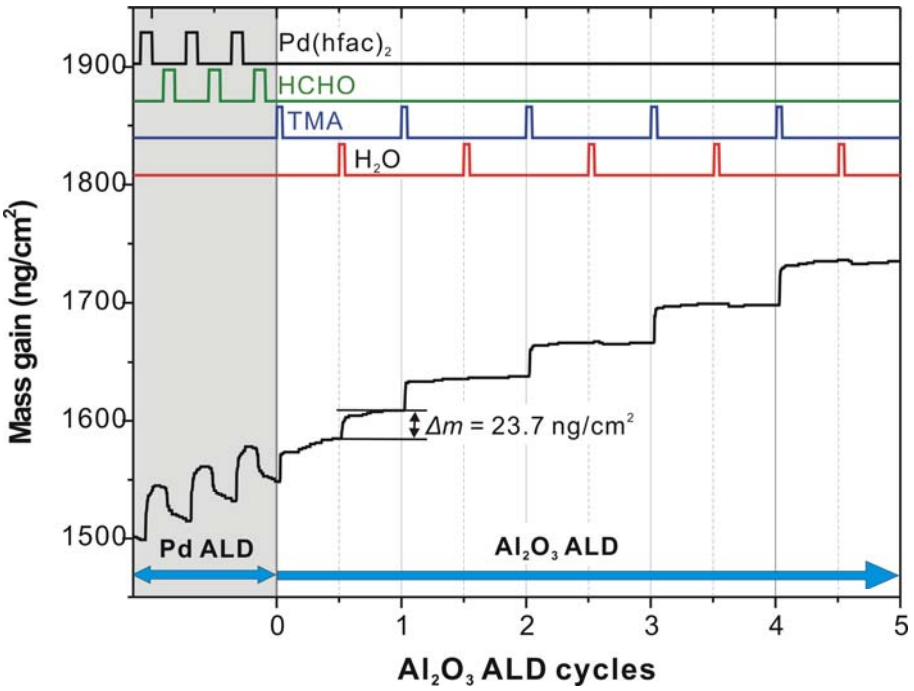

Fig. S1 *In situ* QCM measurements of Al_2O_3 ALD on a Pd NP-coated sensor. Al_2O_3 ALD was carried out after performing 150 cycles of Pd ALD at 473 K. The last 3 cycles of Pd ALD and the first 5 cycles of Al_2O_3 ALD, togther with the exposure sequences of the Pd and Al_2O_3 ALD precursors, are shown here. The first Al_2O_3 ALD cycle on the Pd surface is characterized by an anomalously large mass gain of 23.7 ng/cm^2 during the H_2O exposure.

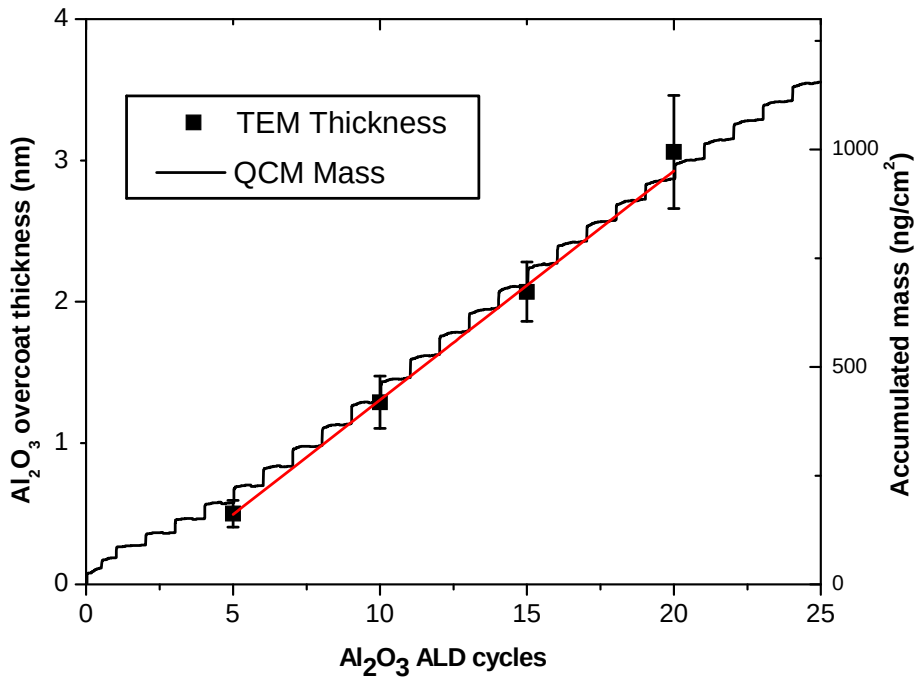

Fig. S2 *In situ* QCM mass gain measurements for Al_2O_3 ALD on a Pd NP-coated sensor (black line) compared to ALD Al_2O_3 thickeness measurements obtained from TEM (from Fig. 5f, solid squares).

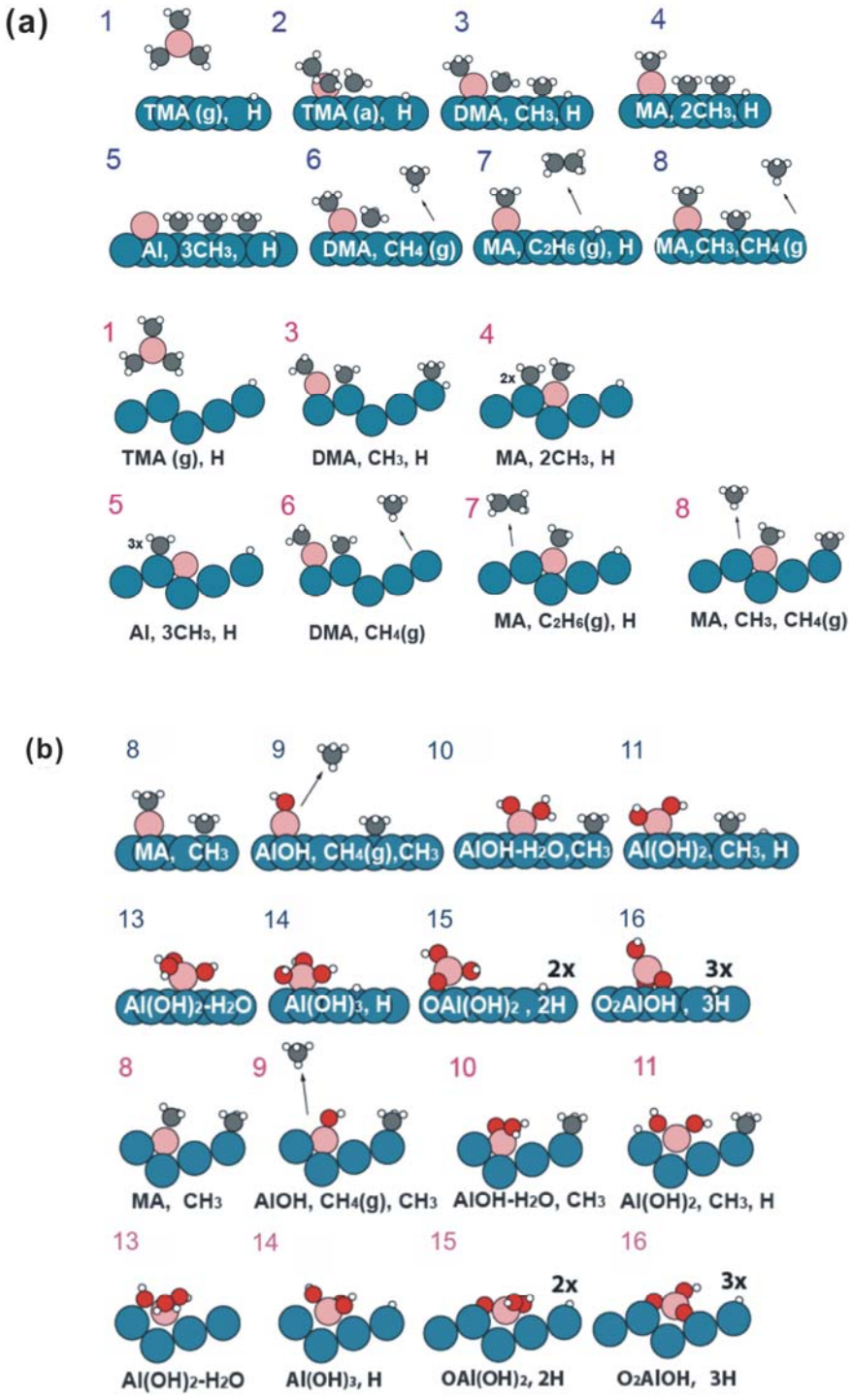

Fig. S3. Schematic representations of surface geometries on Pd(111) (a) and Pd(211) (b) surfaces.