# Supplementary Materials: Design of Molecular Water Oxidation Catalysts Stabilized by Ultrathin Inorganic Overlayers—Is Active Site Protection Necessary?

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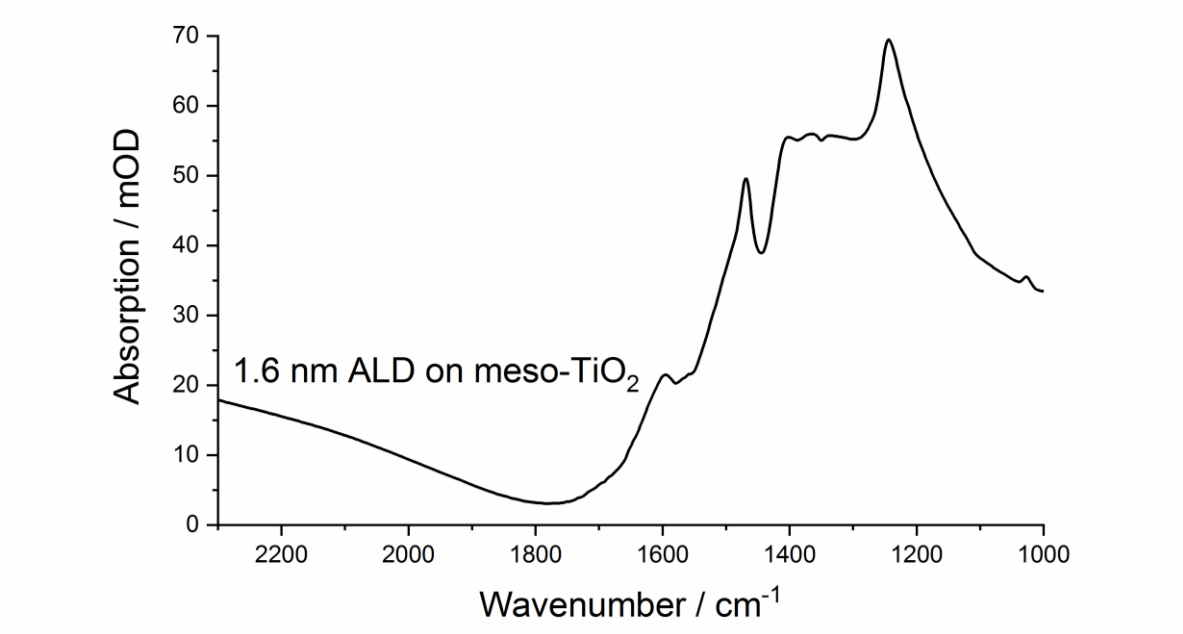


**Figure S1**. IR spectrum of meso-$TiO_2$ with 1.6 nm (30 cycles) of ALD-$TiO_2$.

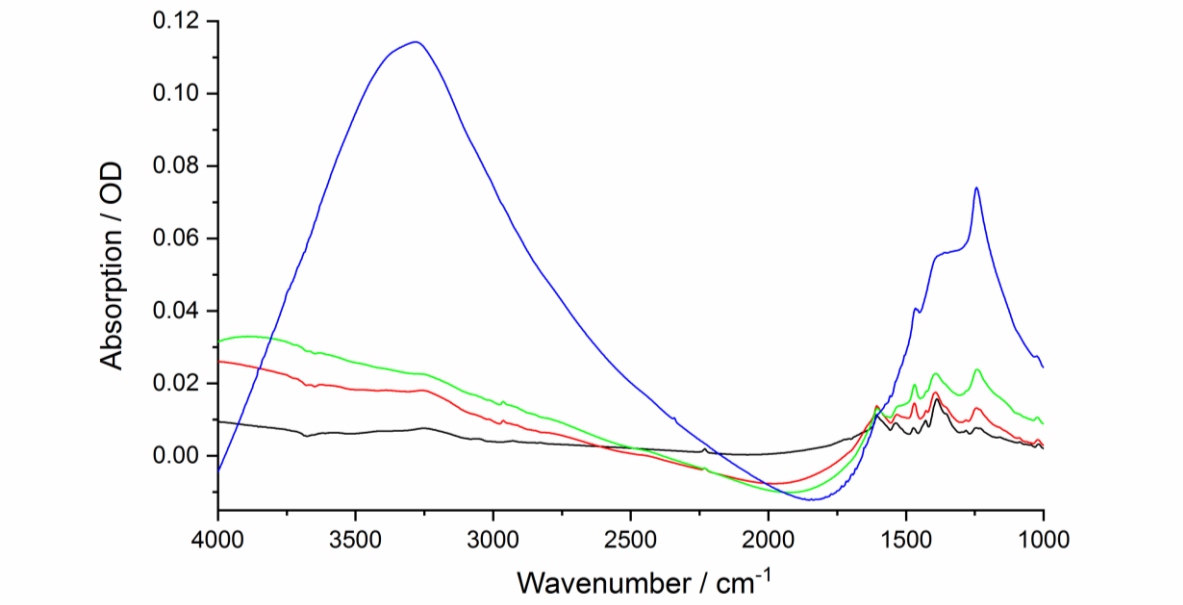


**Figure S2**. IR spectra of anchored Ru–Cl on meso-$TiO_2$ without overlayer (black), with 10 cycles (red), 30 cycles (green) and 80 cycles (blue) of ALD-$TiO_2$. The increasingly large baseline shifts are due to interference within the mesoporous layer.

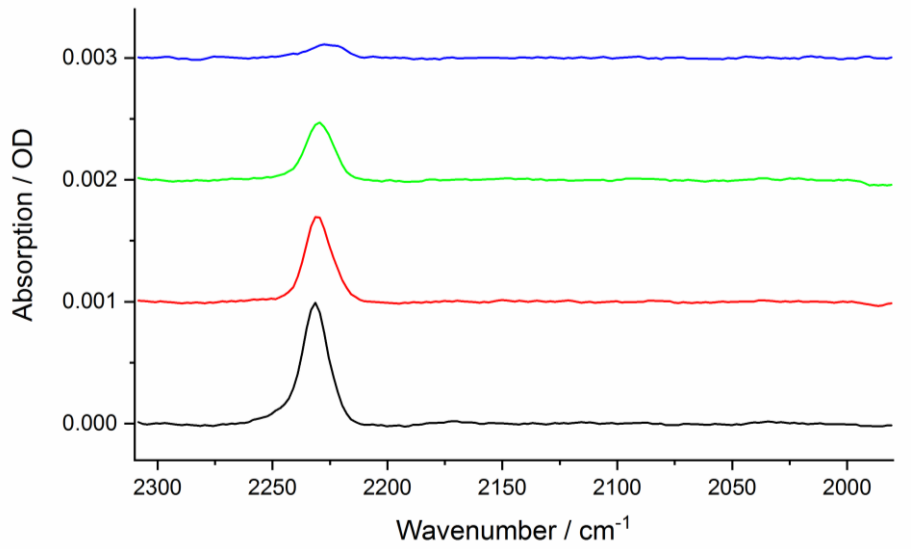


**Figure S3**. IR spectra of anchored Ru–Cl on meso-$TiO_2$ before deposition of ALD-$TiO_2$ (black), after 10 cycles (red), 30 cycles (green) and 80 cycles (blue).

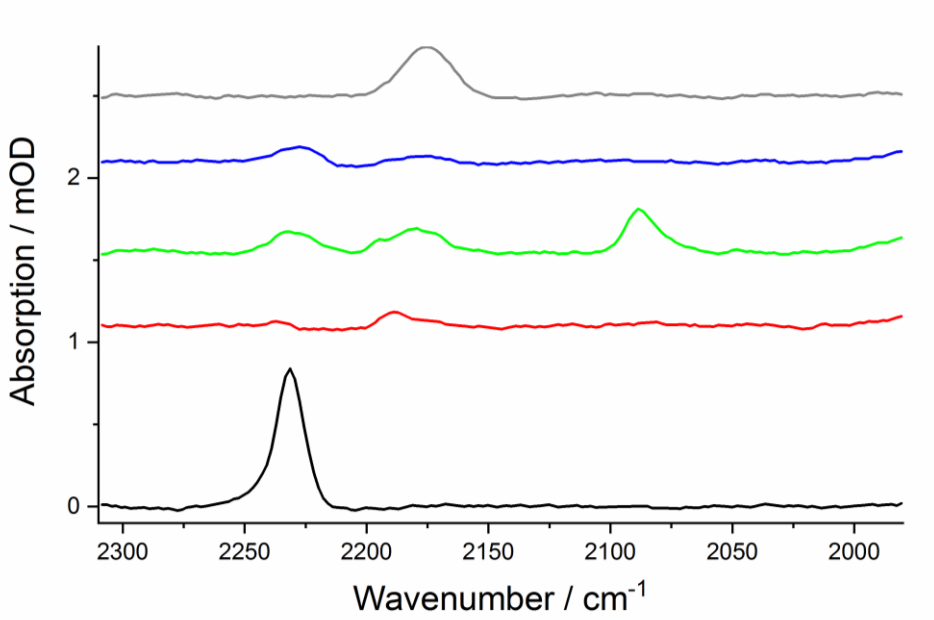


**Figure S4**. IR spectra of anchored Ru–Cl on meso-$TiO_2$ (black) and ALD-protected Ru–Cl on meso-$TiO_2$ after NaCN treatment with 10 cycles (red), 30 cycles (green) and 80 cycles (blue) of ALD-$TiO_2$. A reference of catalyst-free meso-$TiO_2$ with 30 cycles of ALD-$TiO_2$ after NaCN treatment (gray) is shown.

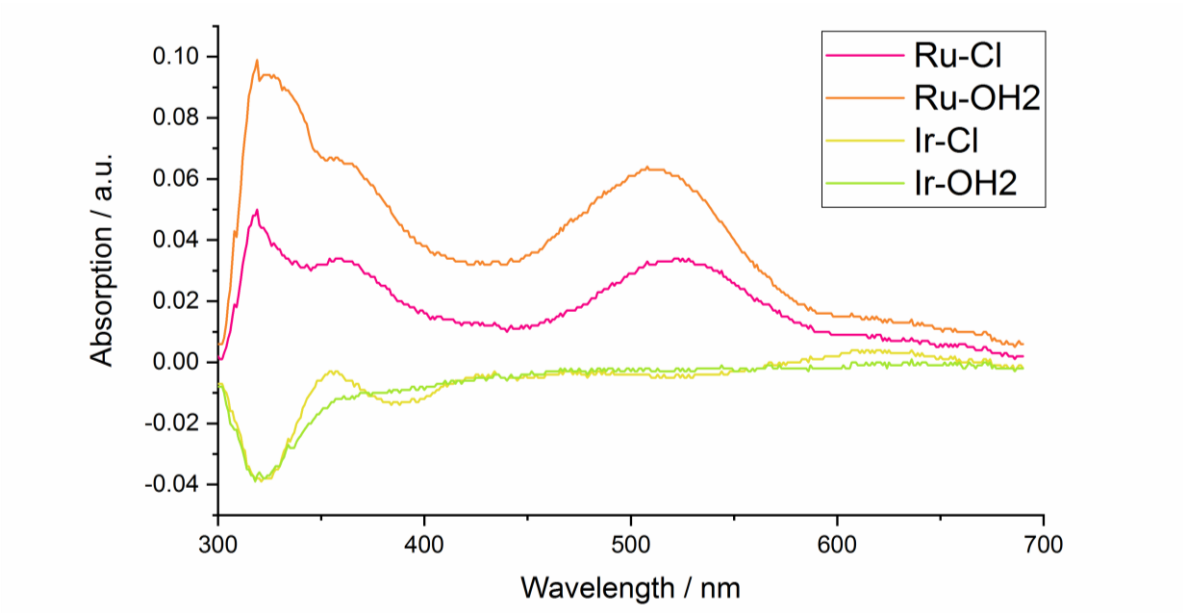


**Figure S5**. UV-Vis Spectra of Ru–Cl, Ru–$OH_2$, Ir–Cl and Ir–$OH_2$ complexes anchored onto meso-ITO. The spectra were obtained after subtraction of unfunctionalized meso-ITO.

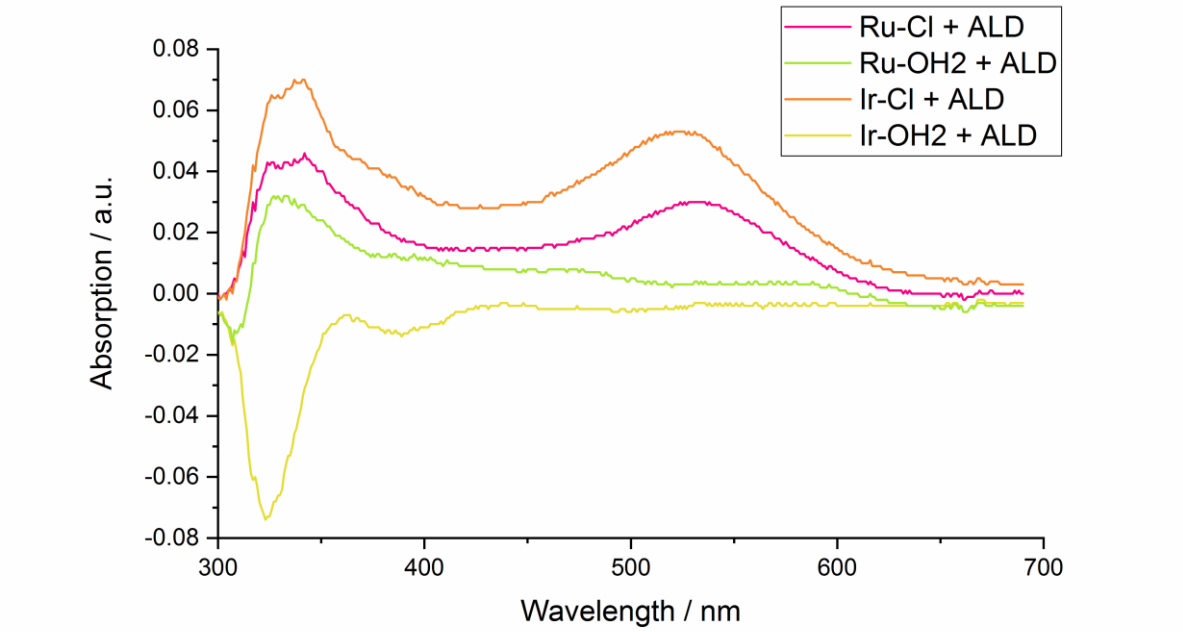


**Figure S6**. UV-Vis spectra of Ru–Cl, Ru–$OH_2$, Ir–Cl and Ir–$OH_2$ anchored on meso-ITO after deposition of 30 cycles ALD-$TiO_2$. The spectra were obtained after subtraction of unfuntionalized meso-ITO with 30 cycles ALD-TiO2.

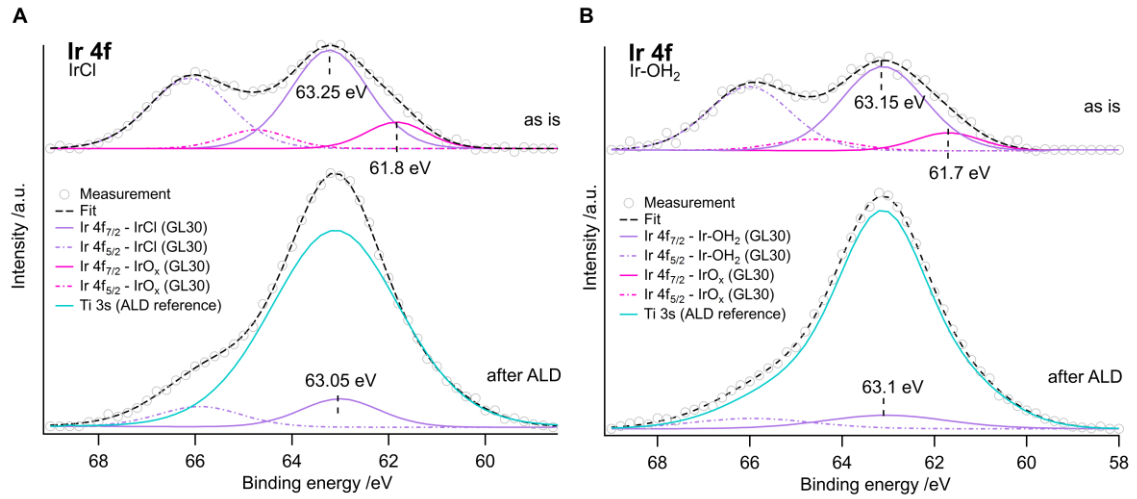


**Figure S7.** XP spectra of (**A**) Ir–Cl and (**B**) Ir–$OH_2$ on ITO before and after deposition of 30 cycles ALD-$TiO_2$. The Ir 4f signals overlap with the Ti 3s signals making interpretation of the Ir 4f signal difficult. For Ir–Cl, comparison with an ALD-$TiO_2$ reference sample reveals a potential contribution of core level emissions from underlying Ir molecules to the spectrum.

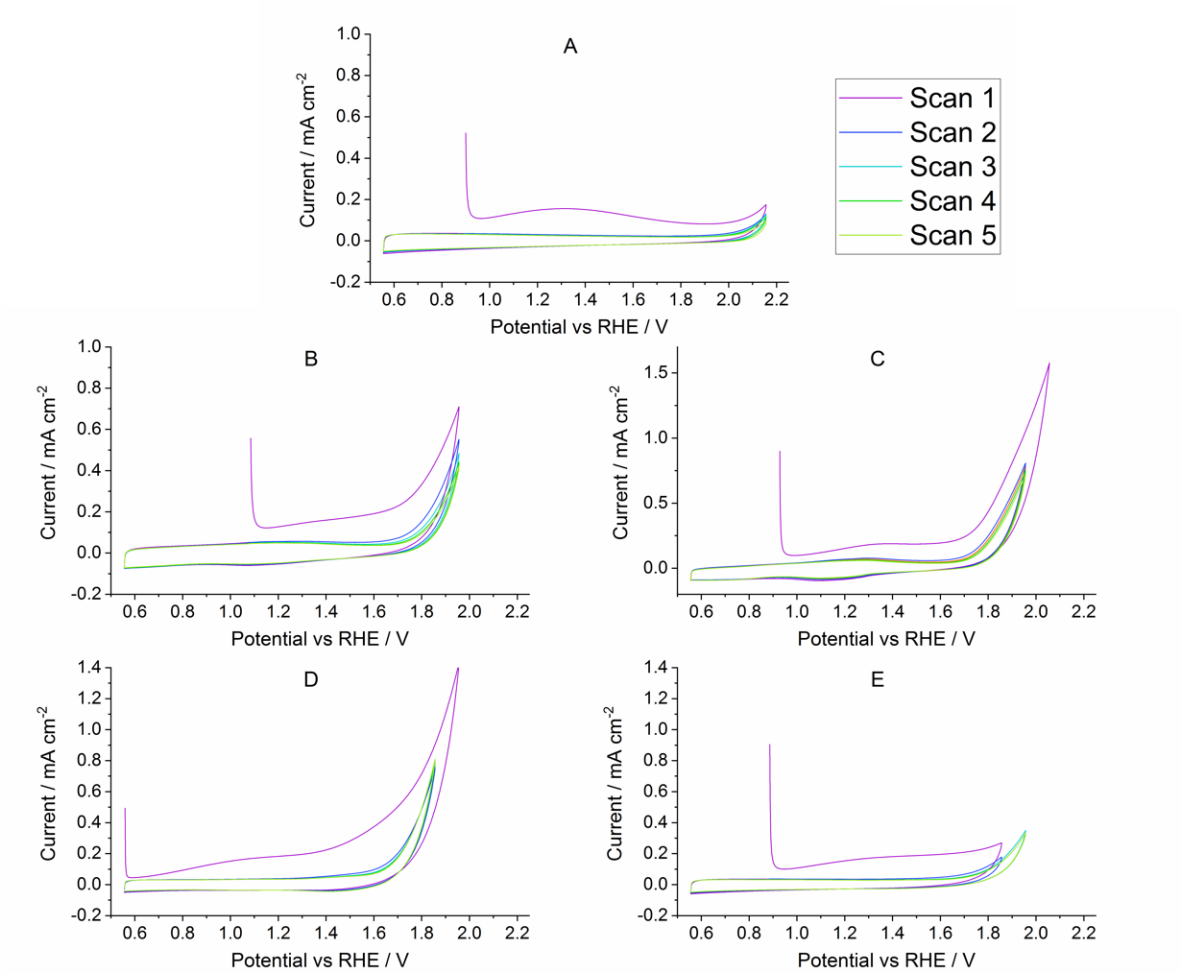


**Figure S8.** First five consecutive CV scans of meso-ITO + 30cycles ALD-$TiO_2$ without molecule (**A**), with Ru–Cl (**B**), Ru–$OH_2$ (**C**), Ir–Cl (**D**) and Ir-$OH_2$ (**E**) in 0.1 $H_2SO_4$. The large current densities observed on the first scan are dominated by capacitive charging of the mesoporous layer.

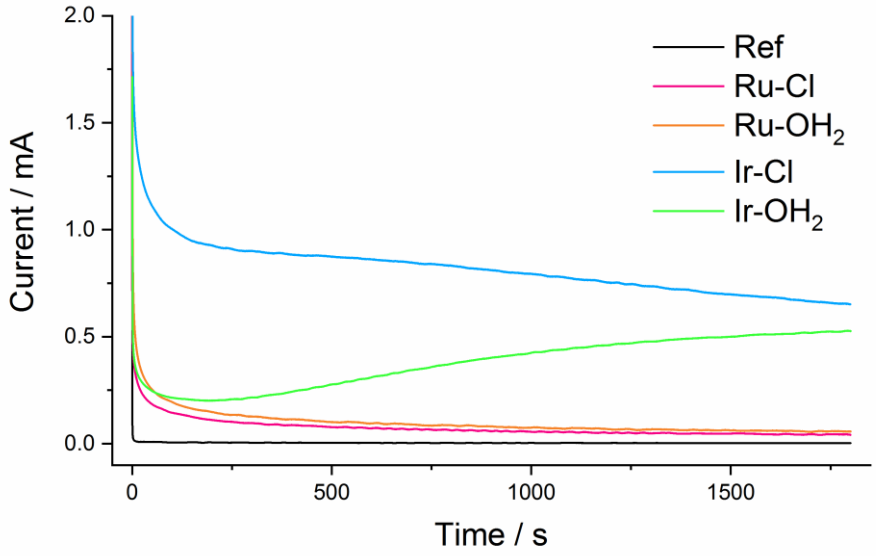


**Figure S9.** Chronoamperometry of Ru–Cl, Ru–$OH_2$, Ir–Cl and Ir–$OH_2$ anchored on meso-$TiO_2$ with 30 cycles ALD-$TiO_2$. Measurements were performed in 0.1 M $H_2SO_4$ at 1.95 V vs. RHE over 30 minutes.