Design of Molecular Water Oxidation Catalysts Stabilized by Ultrathin Inorganic Overlayers – Is Active Site Protection Necessary?

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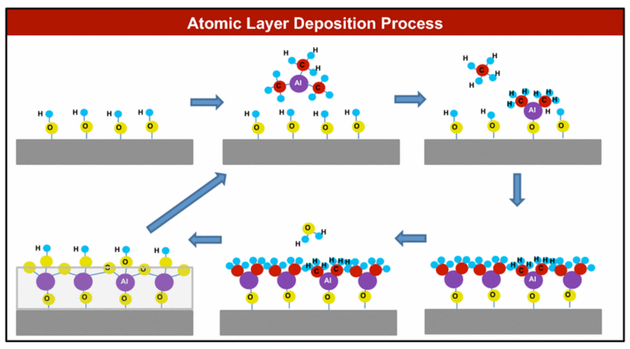
Introduction

Heterogenizing homogeneous catalysts for water splitting

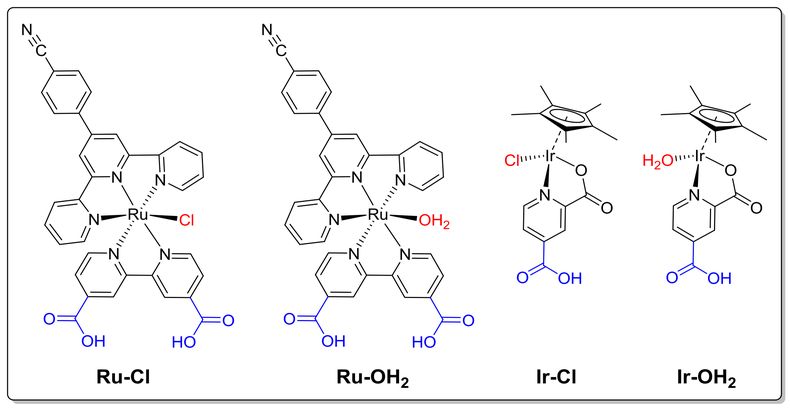
- Homogeneous catalysts are well understood, tunable & easy to analyze
- Heterogenization could transfer these properties to (electrode) surfaces
- Drawback: low stability of anchored molecules (in aqueous solutions)
  → Stabilization by ALD overlayers
- Investigate possible decomposition of anchored molecules during ALD
- Design catalysts with an active site protecting group specifically for post-anchoring ALD protection



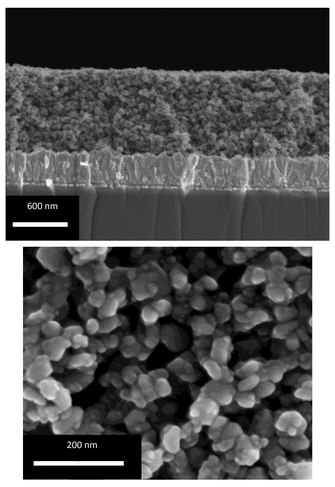
Ultrathin overlayers by atomic layer deposition (ALD):

- metal oxide layers with sub-nanometer resolution
- Requires high temperatures and highly reactive precursors

Materials



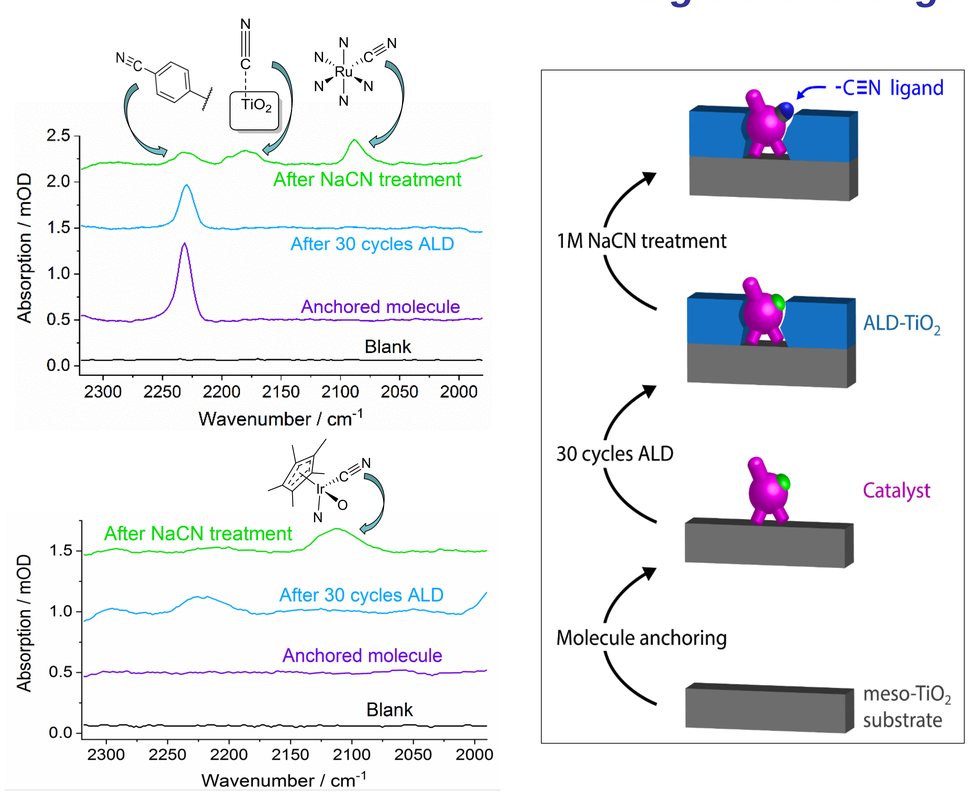
Substrates: Mesoporous TiO_2 and ITO on FTO



Ru and Ir based molecular water oxidation catalysts
→ Chloride protecting group or active aqua ligand (red)
→ Anchoring groups (blue)

Stability vs Activity

Ligand exchange



External reflection IR spectroscopy with transparent mesoporous TiO_2 substrates:

- Optimization of ALD layer thickness
- Accessibility and stability
- Observation of Ru-CN and Ir-CN

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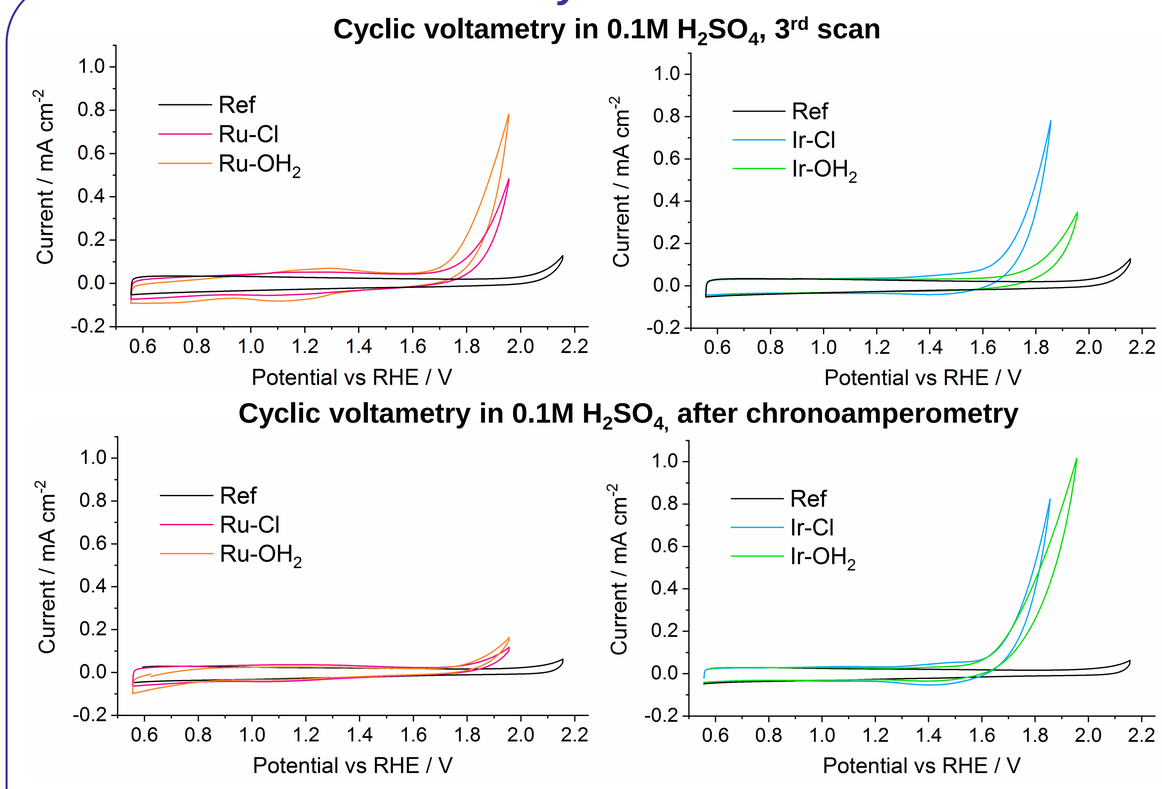
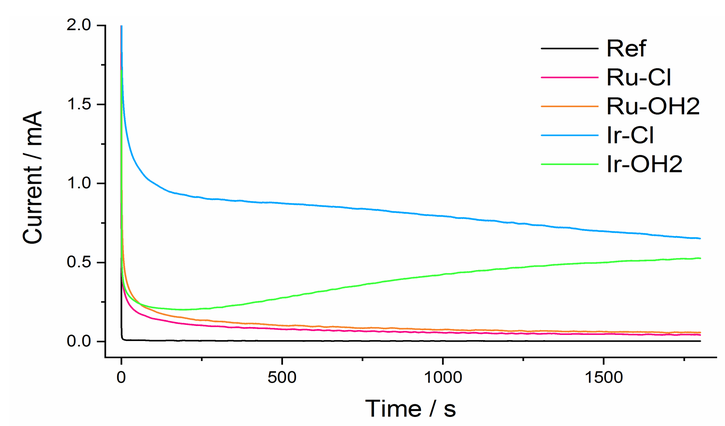
Electrochemical stability

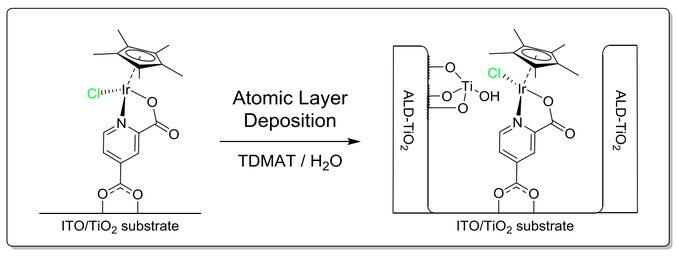




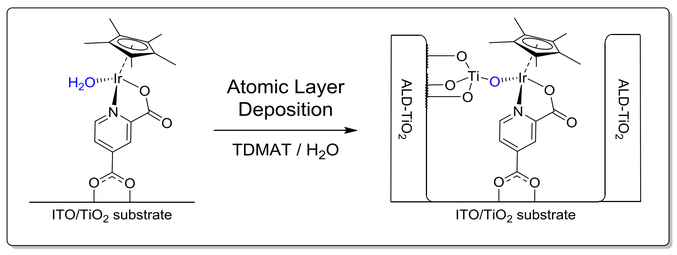
- Ru-Cl and Ru-OH_2 show similar onset, low stability
  → no improvement using Cl ligand
- Ir-Cl has earlier onset than Ir-OH_2 initially
- After 30 mins under bias, Ir-OH_2 activity becomes similar to Ir-Cl
- Good stability of both Ir complexes

Suggested Explanation

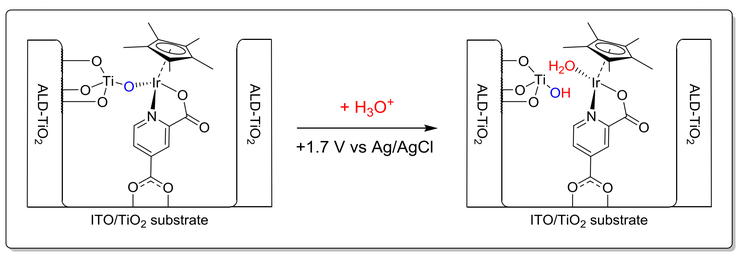
Chloride ligand on Ir-Cl complex does not react with ALD precursor



Aqua ligand on Ir-OH_2 partially reacts with TDMAT
→ Deactivation of catalyst – higher overpotential



Under operating conditions, aqua ligand can be regenerated



Conclusions

- Molecular catalysts can be stabilized using ALD
- For some complexes, using a Cl as a protecting group can be a viable strategy to keep active site free
- In case of Ir-OH_2, the active site may react and be passivated but then revert back to an active form when strong electrical bias is applied

References

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