Selective ALD of metal-oxides on noble metals through catalytic oxygen activation

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Introduction

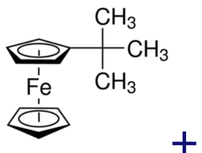
Iron oxide (FeO_x) and **nickel oxide (NiO_x)** find applications in catalysis, magnetic storage, solar cells, etc.

Often combined with noble metals like **platinum (Pt)** and **iridium (Ir)**, for example **Fe/Pt** alloys.

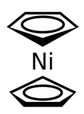
Atomic layer deposition (ALD) of FeO_x / NiO_x requires **strong** oxidizing reactants (O_2 plasma, ozone).

Selective ALD on catalytic substrates

t-butyl ferrocene (TBF) ~250-300 °C



nickelocene ($NiCp_2$) ~250 °C



+ O_2 gas →

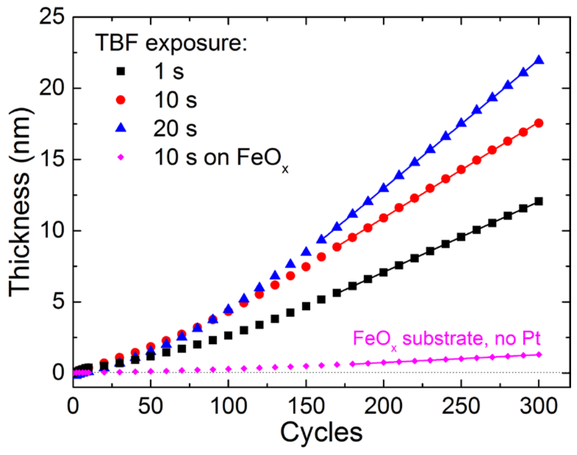
Selective deposition, only on **catalytic noble metals** (Pt / Ir)

No growth on Si / SiO_2 / Al_2O_3

Deposition possible because of **dissociative chemisorption** of O_2 on Pt / Ir

Ellipsometry results

In-situ spectroscopic ellipsometry (SE) **FeO_x on Pt:**

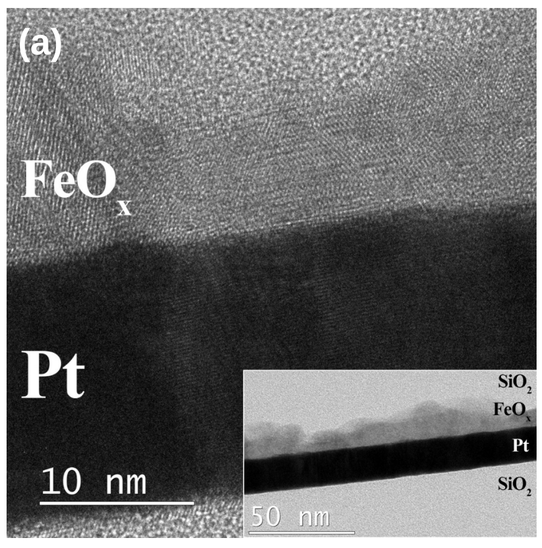


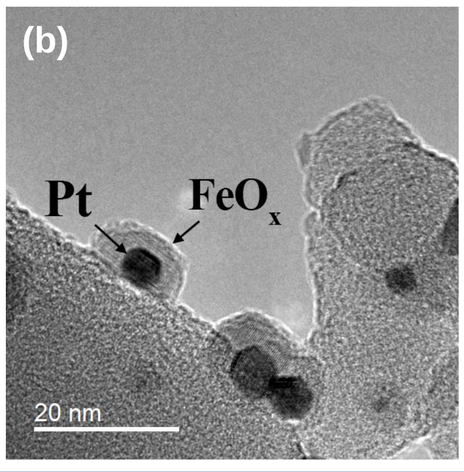
- Linear growth between 0.5 – 0.9 Å/cycle
- Almost no growth on FeO_x substrate with **no Pt**
- **Pt still catalytic even after >20 nm FeO_x coverage?**

TEM analysis

(a) Planar films: FeO_x on Pt

- 300 cycles selective FeO_x ALD
- Well-defined interface
- FeO_x crystalline
- Closed film, but high roughness





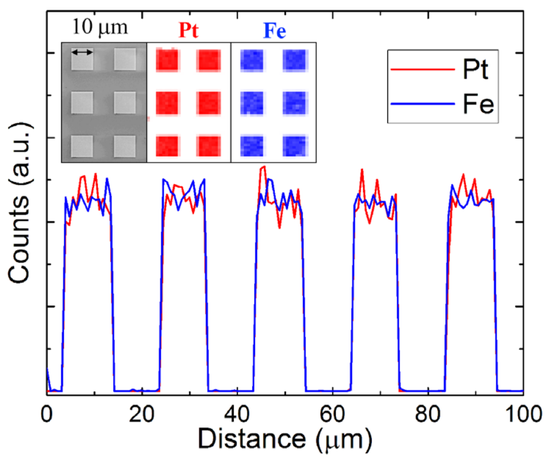
(b) Core-shell Pt-FeO_x particles

- 50 cycles selective FeO_x ALD
- Closed shell of FeO_x selectively deposited on Pt core

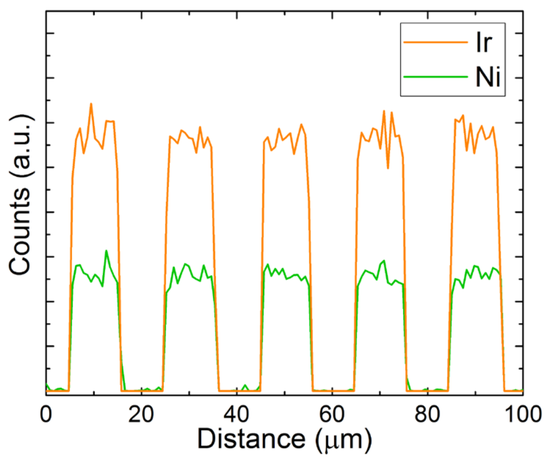
AES on patterned substrates

Deposition on Pt / Ir patterned squares demonstrate excellent selectivity

FeO_x on Pt squares

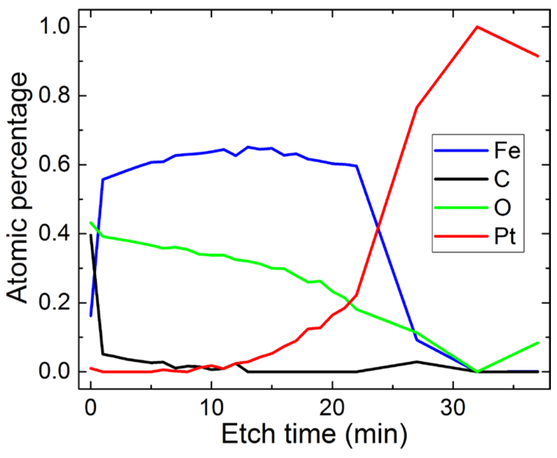


NiO_x on Ir squares

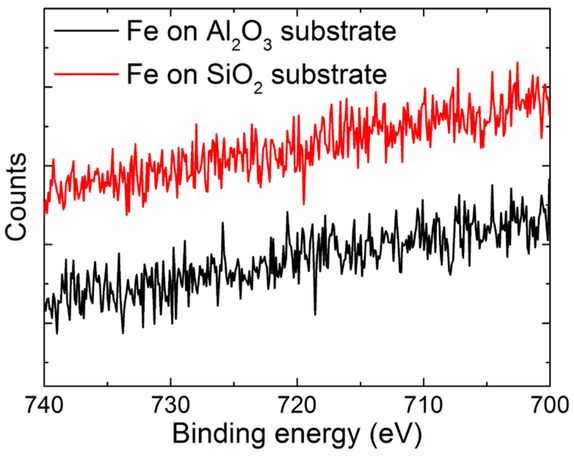


XPS analysis

XPS depth profile shows separate FeO_x and Pt layers



Fe2p scans on SiO_2 / Al_2O_3 after 300 cycles → **no growth**



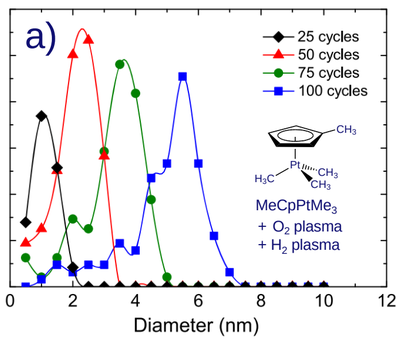
Growth of carbon nanotubes (CNTs)

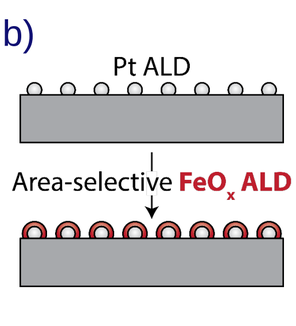
a) Pt ALD for nanoparticles

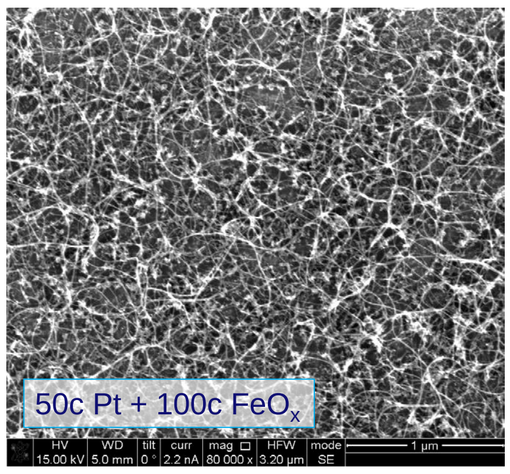
- Diameter control by number of cycles

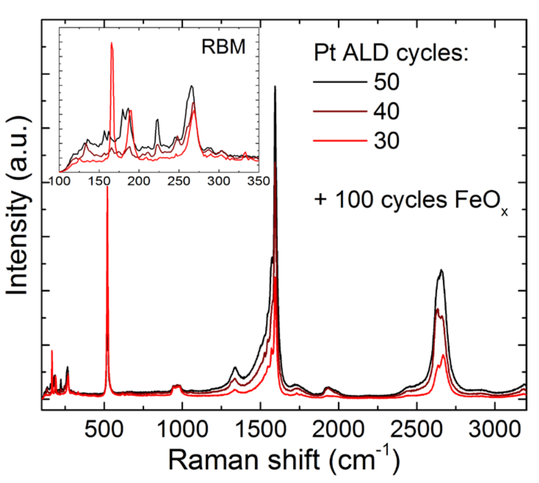
b) Selective FeO_x ALD on Pt particles:

- Fe/Pt alloyed particles show high activity for CNT growth
- **No CNTs** with just Fe or just Pt.









Conclusions

Demonstrated **selective ALD** of **FeO_x / NiO_x** by activation of O_2 gas on **catalytic Pt / Ir.**

Prepared **thin films** and **core-shell** nanoparticles.

Excellent selectivity, no growth on $Si/SiO_2/Al_2O_3$.

Mechanism not fully clear → still growth after **full coverage** of the catalytic substrate?

Possibly applicable to **wide range of materials**.

Fe/Pt nanoparticles highly active for **CNT growth**.

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