Microplasma-based synthesis of nanostructured Pt

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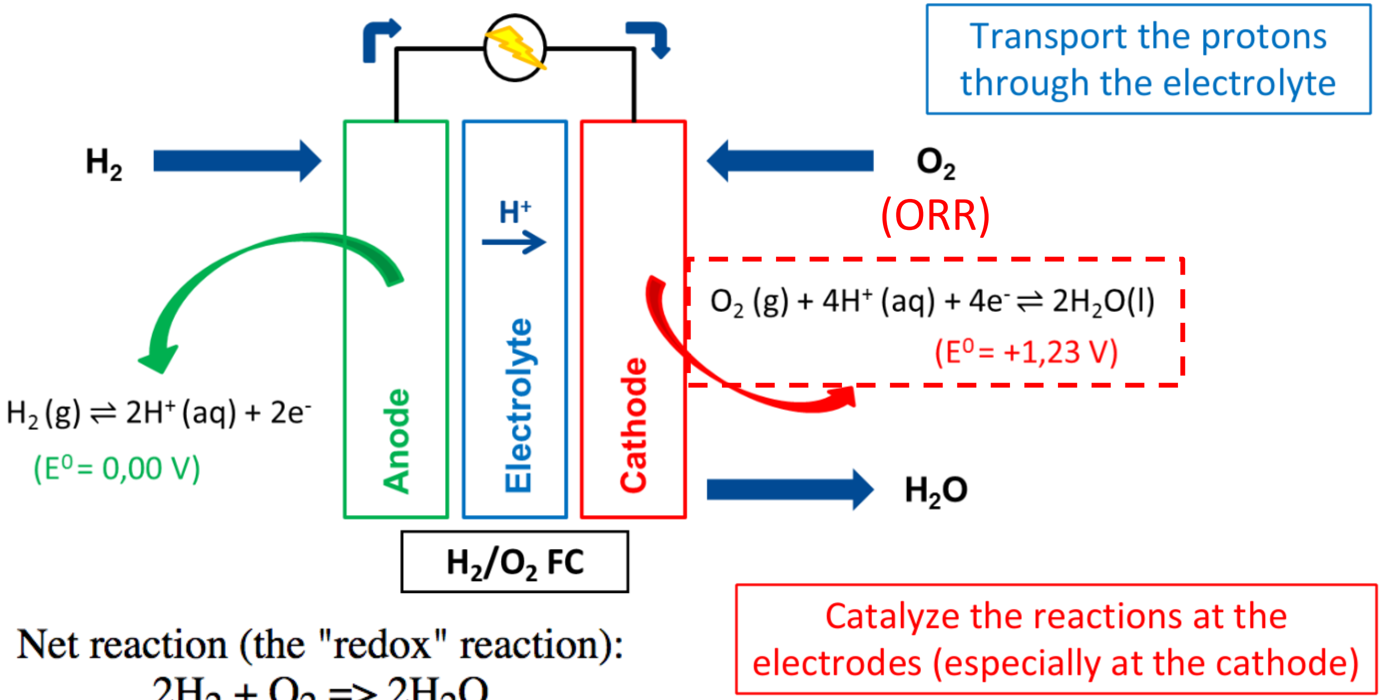
Nanostructured Pt Films for H_2 based Fuel Cell



Net reaction (the "redox" reaction):

$2H_2 + O_2 \Rightarrow 2H_2O$

$E^o = +1.23V$

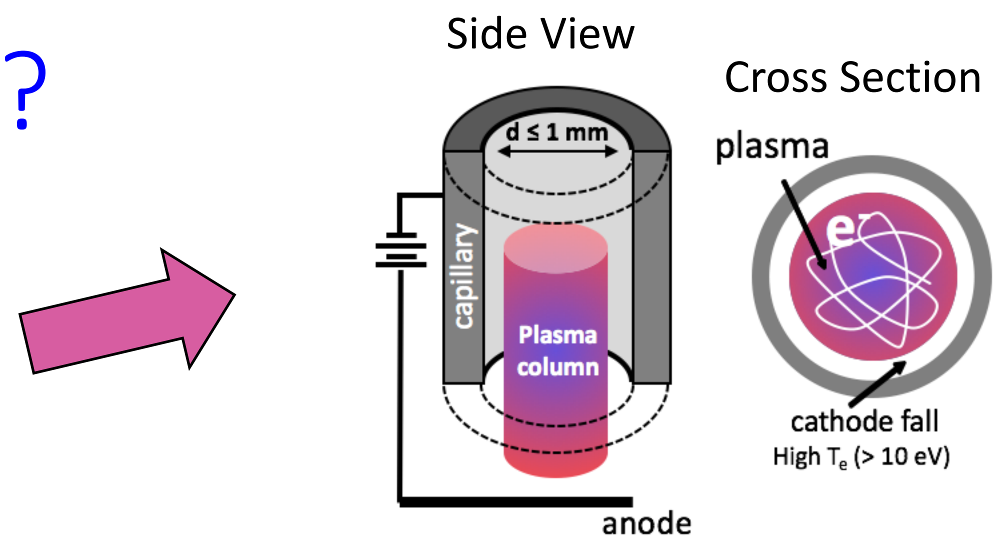
- Fuel Cell: Produces electricity through electrochemical reaction
- $2H_2 + O_2 \rightarrow 2H_2O$
- Fuel cells rely on Pt as a catalyst for oxygen reduction reaction (ORR)
- Platinum is an **expensive** metal → Use Pt more efficiently → Increase surface area, alloy Pt with other metals

Project Goals

- Utilize novel methods to deposit Pt nanoparticles for fuel cell catalysts → ***microplasmas***
- Explore how plasma operating parameters affect Pt deposition:
  - Pressure
  - Pt-precursor Flux
  - Substrate type
  - Electrical configuration
- Characterize Pt films and nanoparticle morphology
- Investigate if Pt can alloyed with Ni
  - Can PtNi be deposited directly and is PtNi catalytically active for ORR?

What is a microplasma?

- Dense plasma confined to very small space → 10 μm – 1 mm



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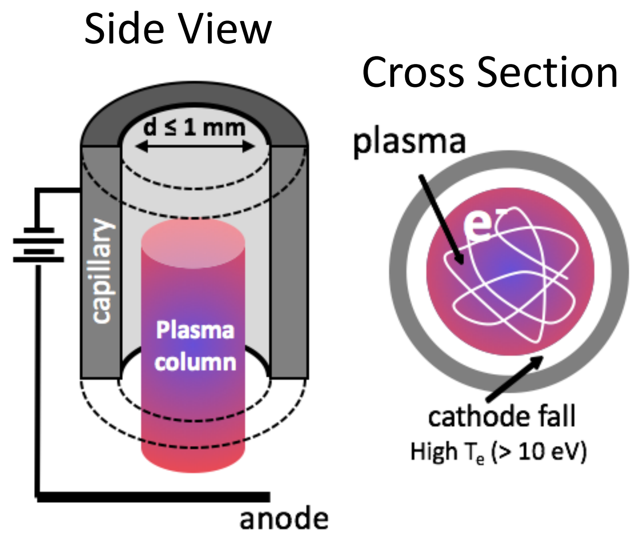
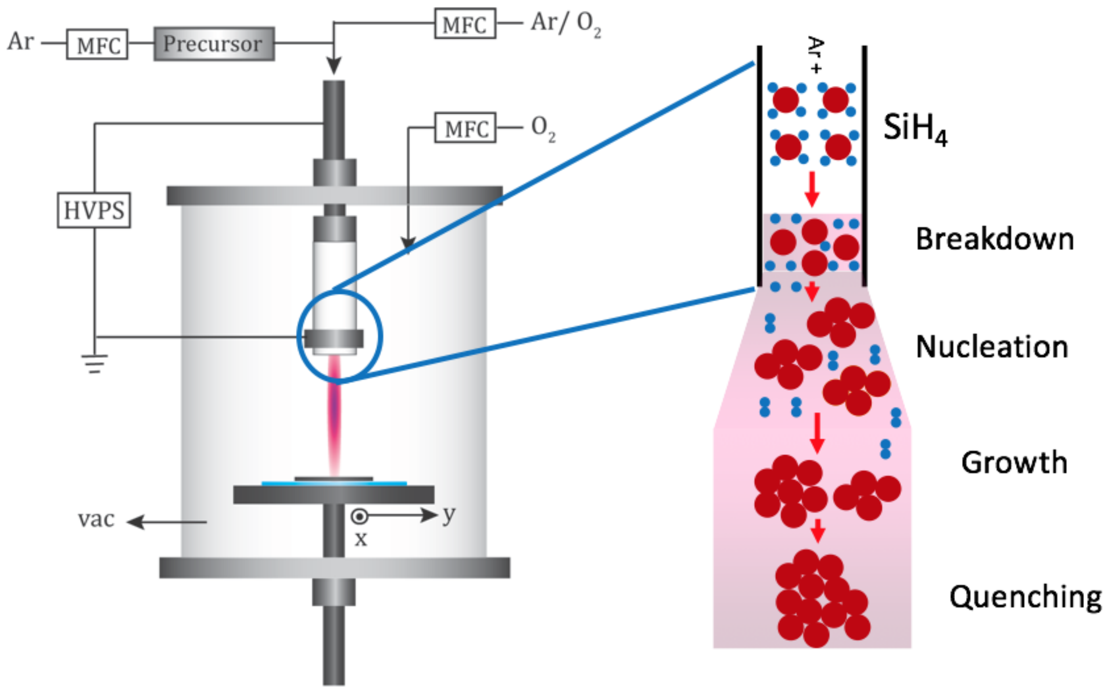
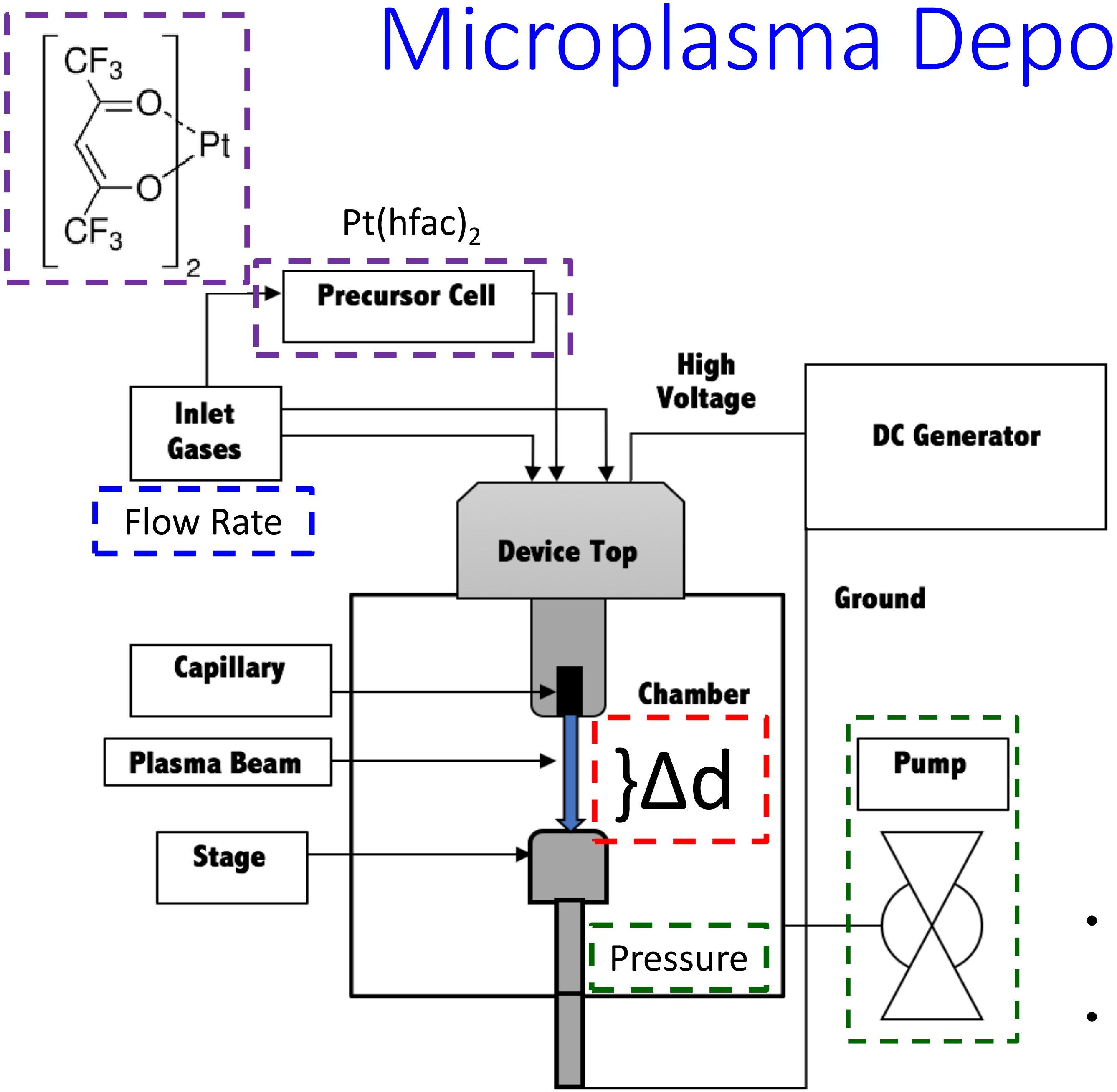


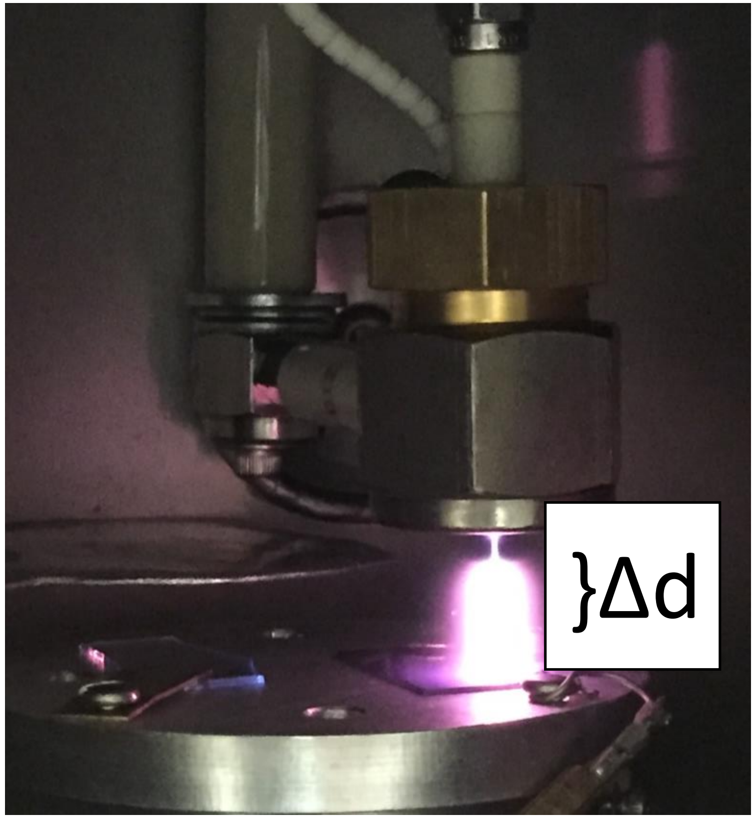
- Advantages
  - Spray deposit nanostructured materials on any substrate
  - Grow particles to nano/micro structured sizes
  - Tune particle composition → make alloys



Microplasma Deposition Reactor



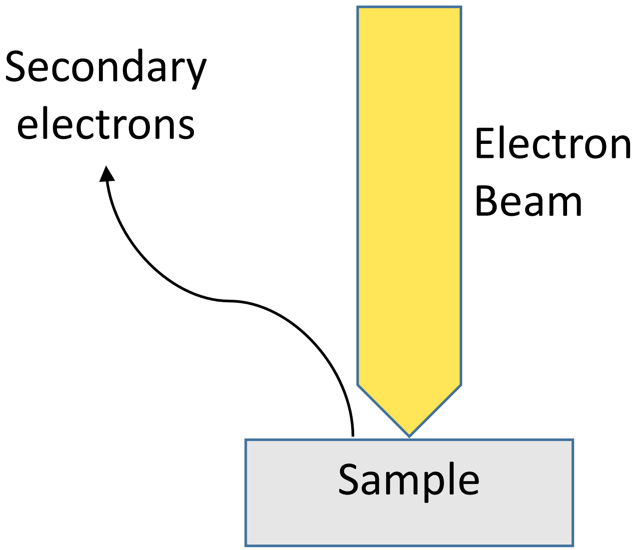
Pressure = 50 torr



- High voltage (plasma) discharge struck between capillary and substrate
- **Control Parameters**: gas flow rate, pressure, precursor, capillary-stage distance, cell temperature (for sublimation)

Characterization of Samples

Scanning Electron Microscope **(SEM)**
Morphology & thickness



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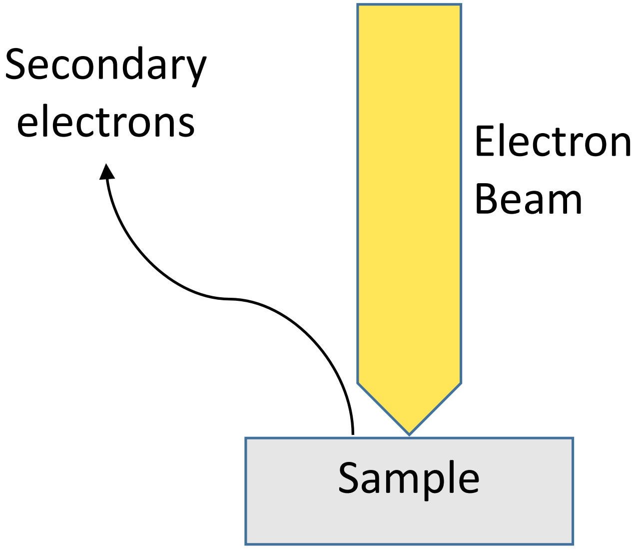
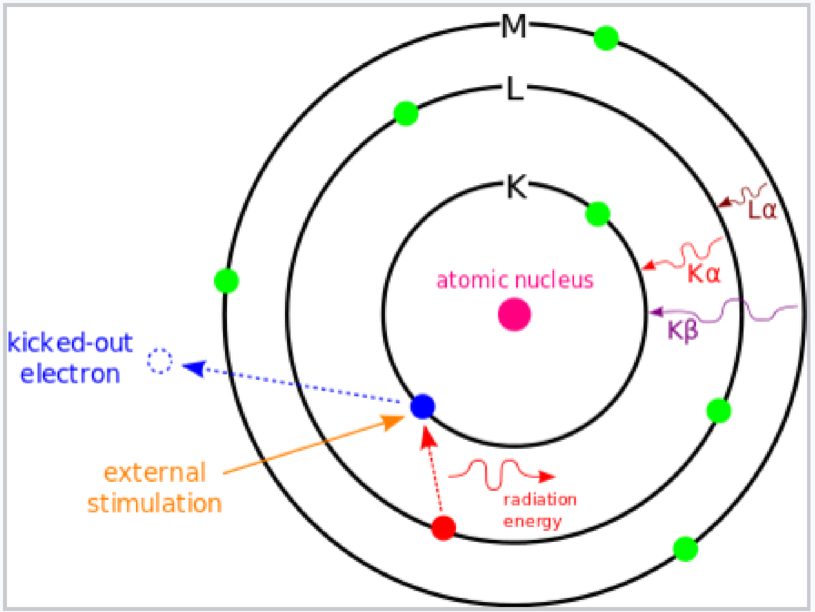


Energy Dispersive X-ray **(EDX)**
Film elemental composition



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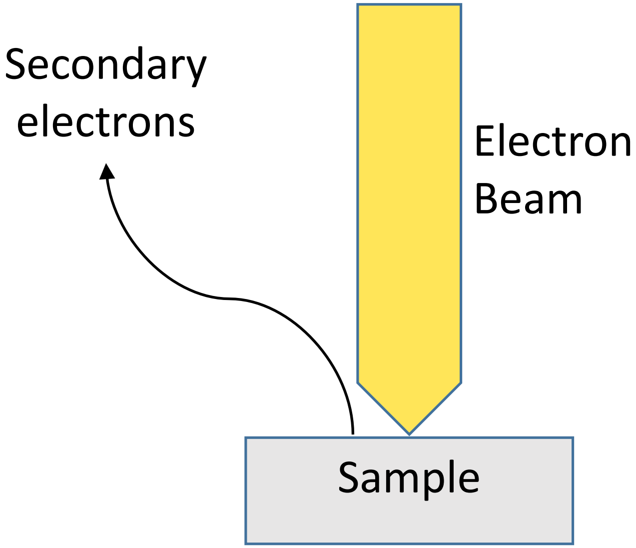

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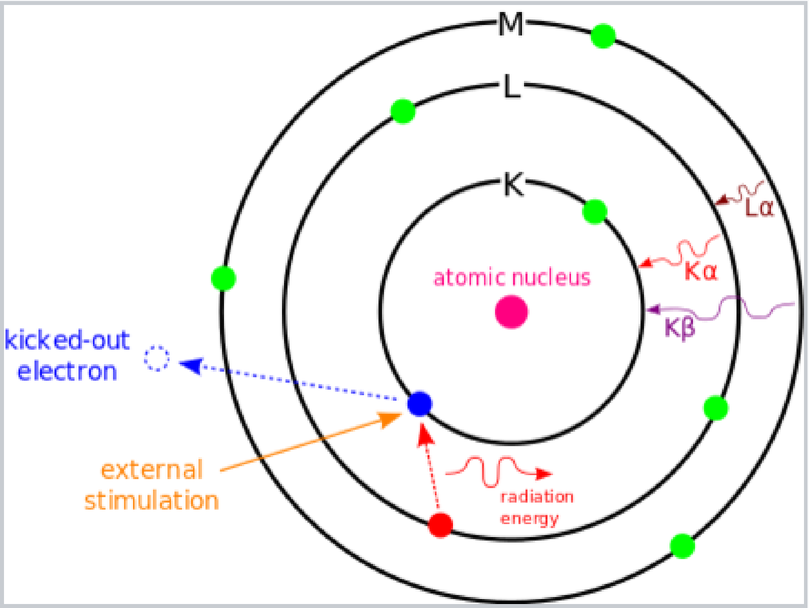
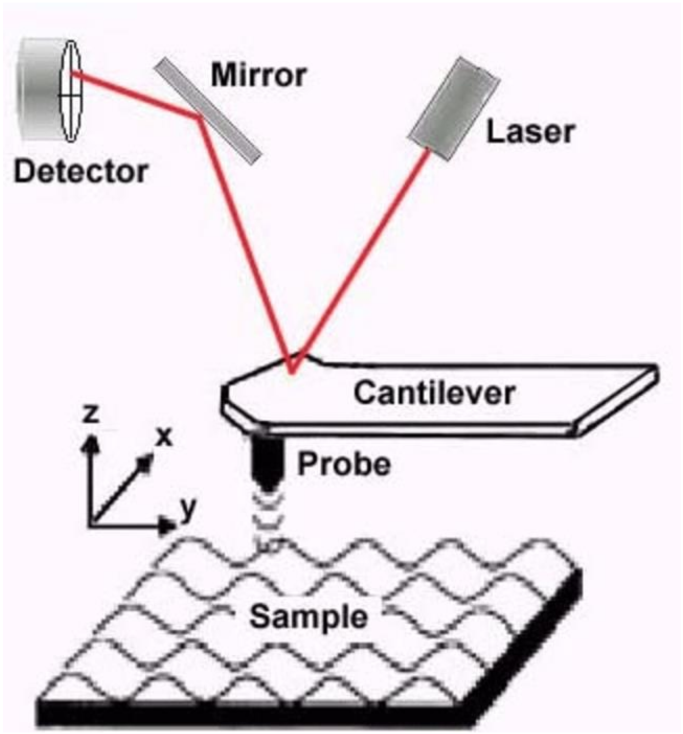
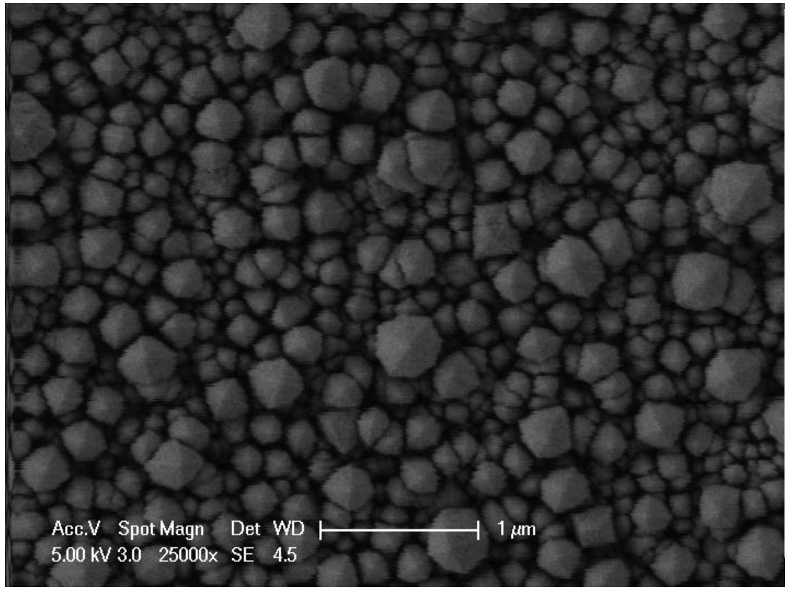


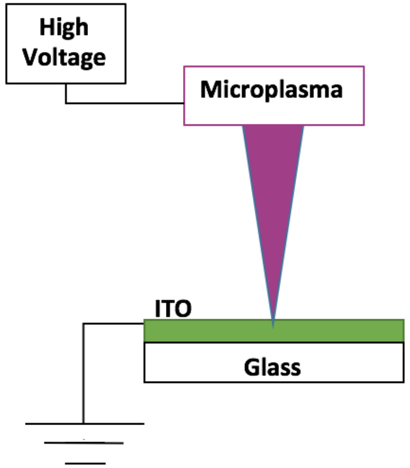
Atomic Force Microscope **(AFM)**
Surface topography



Pt film morphology: Substrate Effect at P = 760 torr

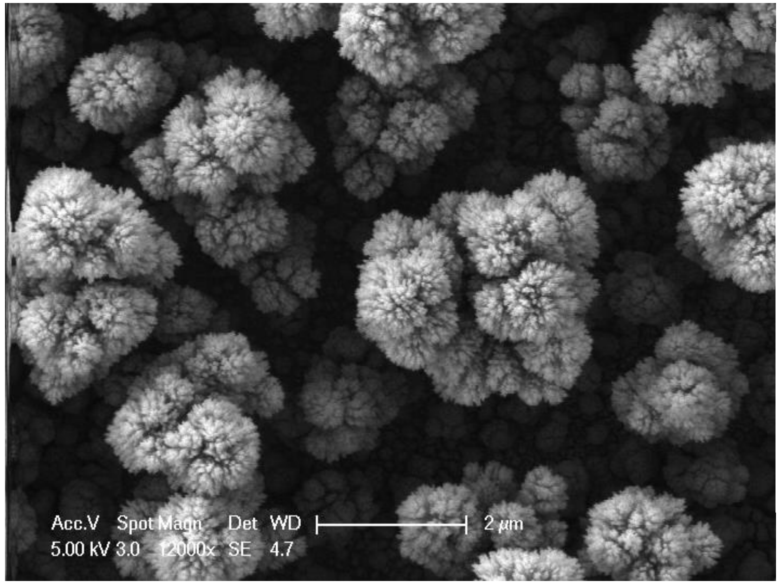
Substrate: Indium Tin Oxide (ITO)

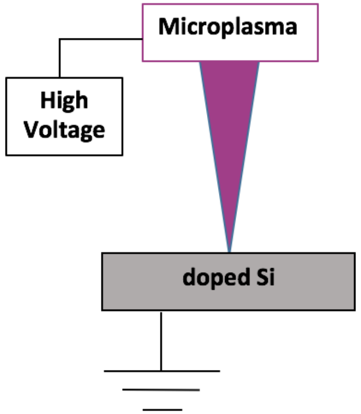




crystal facets→ fcc Pt

Substrate: Doped Silicon(Si)





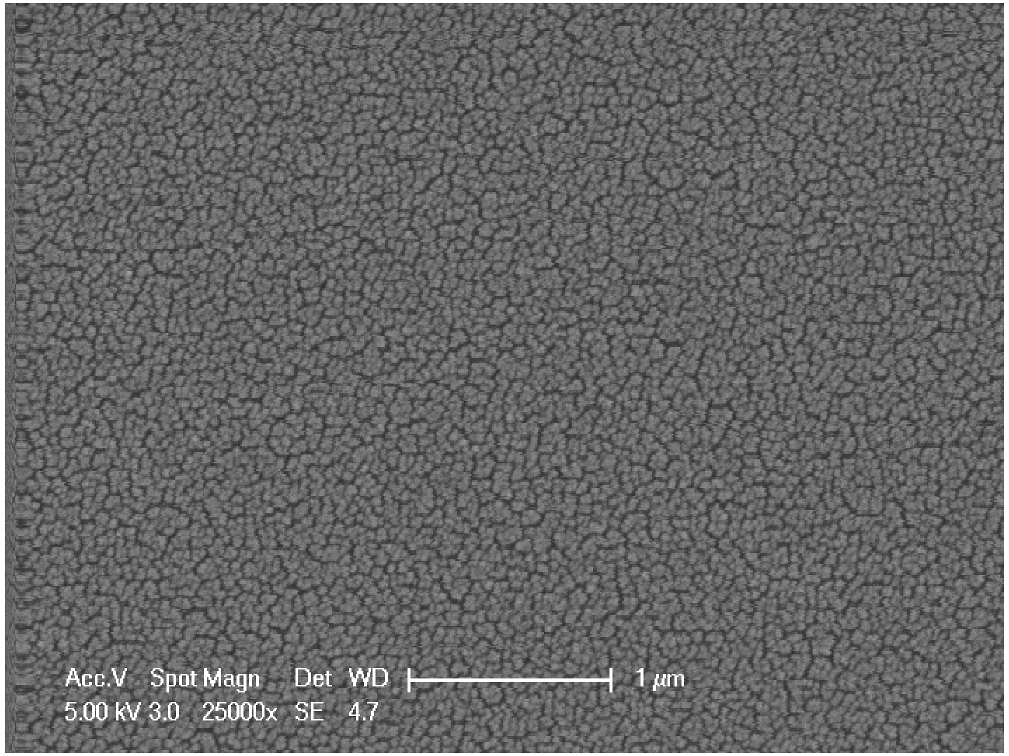
Porous deposit, ‘ballistic’ aggregation

- Substrate type affects morphology
- How plasma current travels to ground affects morphology (thin ITO film vs. Si subst)

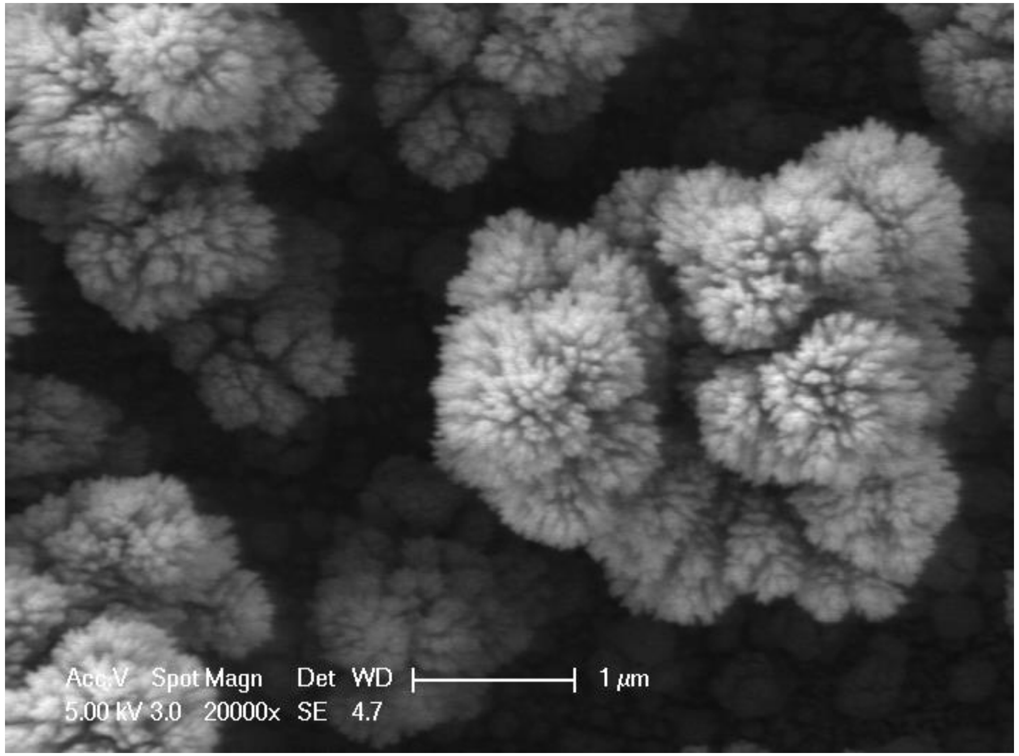
Control: P = 760 torr,
t = 30 min,
T_{Pt} = 45^{o}C
Δd = 3 mm

Pt film morphology: Pressure Effects

P = 50 torr



P = 760 torr (atm pressure)



- Pressure significantly affects deposition process and film morphology
- Lower pressure = **lower Pt-precursor flux** → thinner film
- Higher pressure → ballistic-like aggregation of 'clusters', more porous

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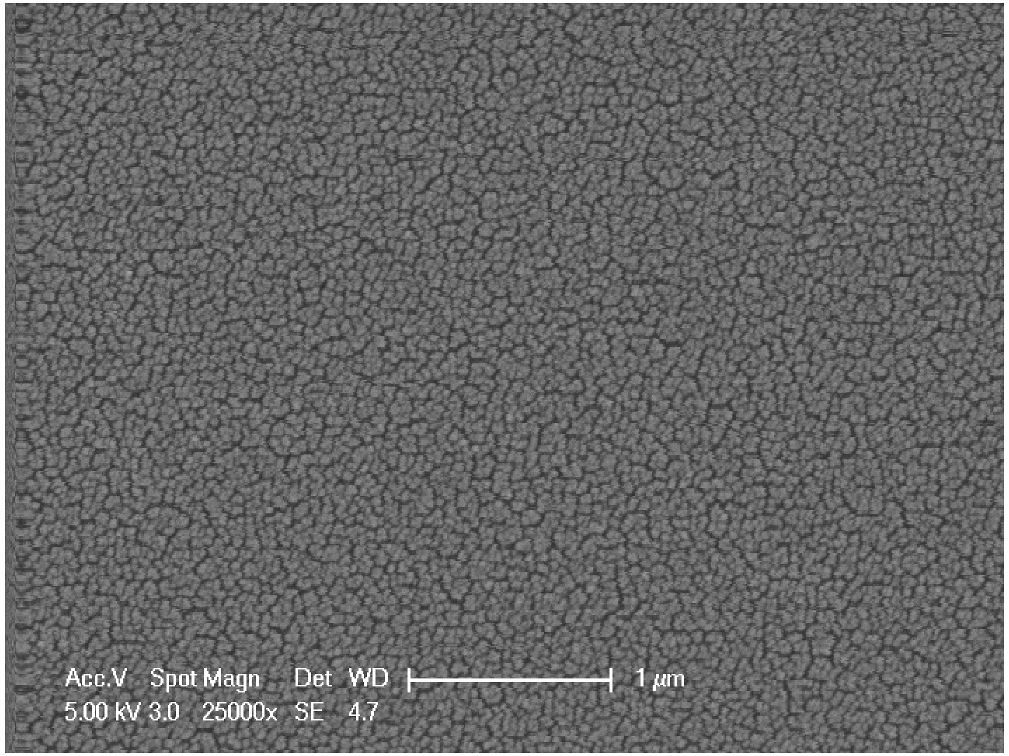

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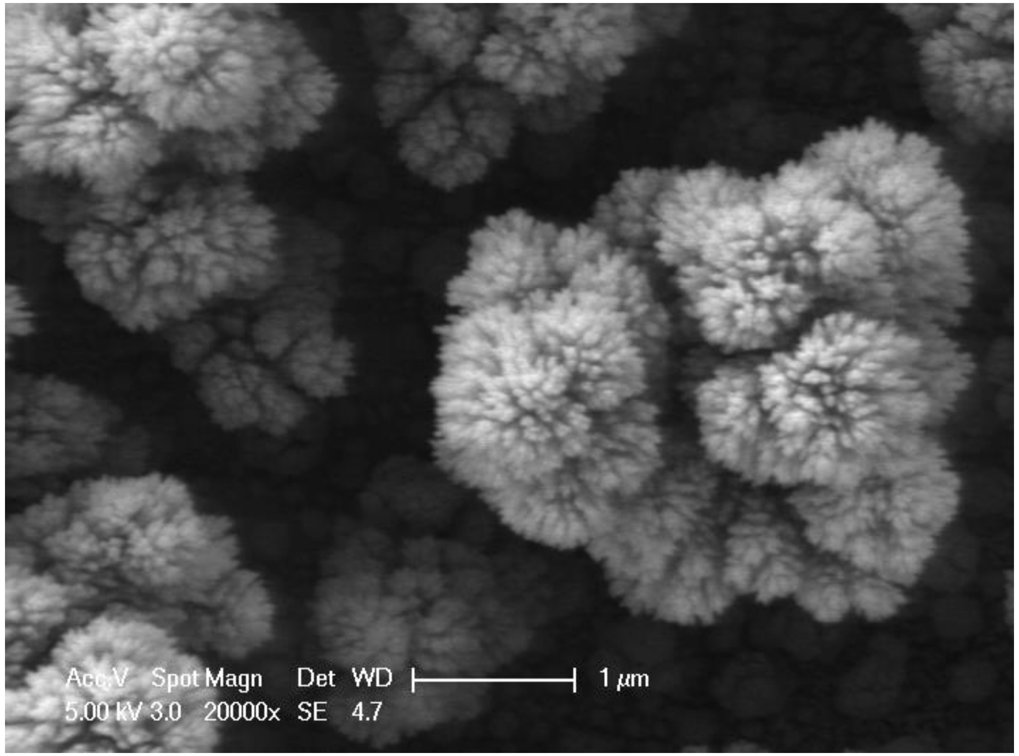

- Pressure significantly affects deposition process and film morphology
- Lower pressure = **lower Pt-precursor flux** → thinner film
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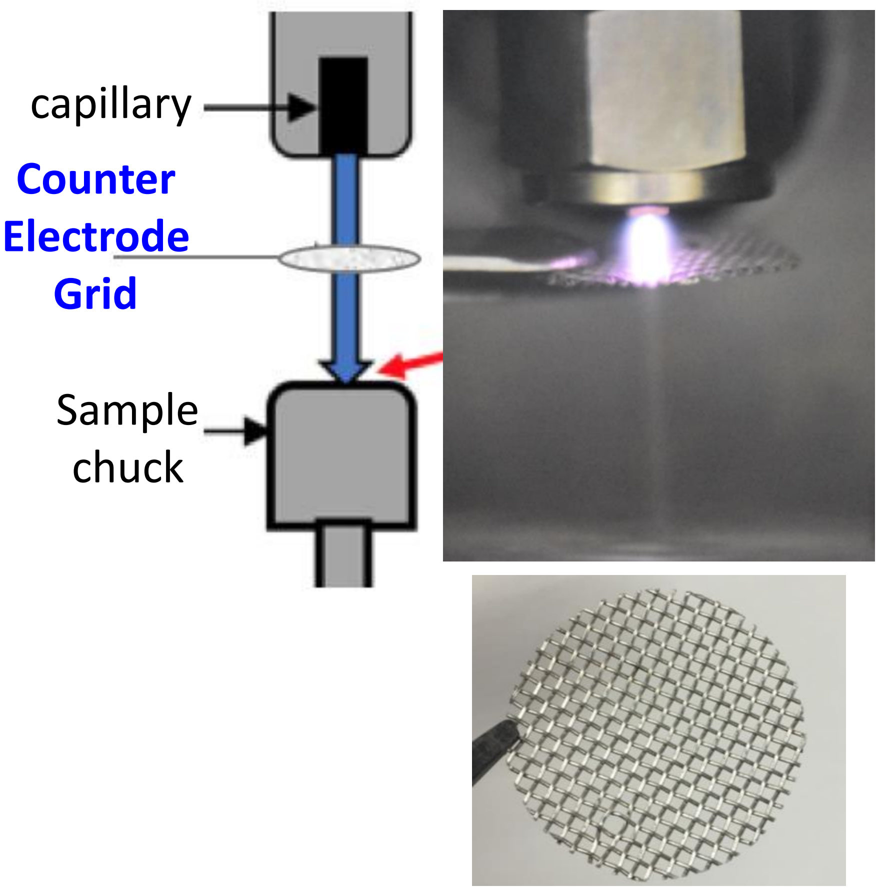
- Jet-substrate distance too small → **move farther away + new counter-electrode**

Control:
Substrate: Si,
t = 30 min,
T_{Pt} = 45°C
Δd = 3 mm

Pt Nanoparticle Deposition

- Larger capillary substrate distance needed → **New counter electrode**



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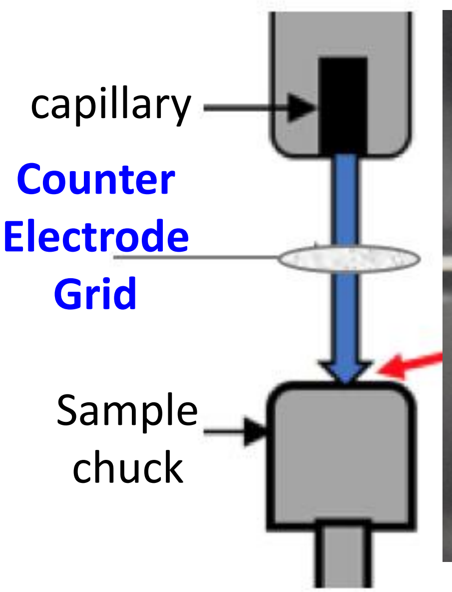
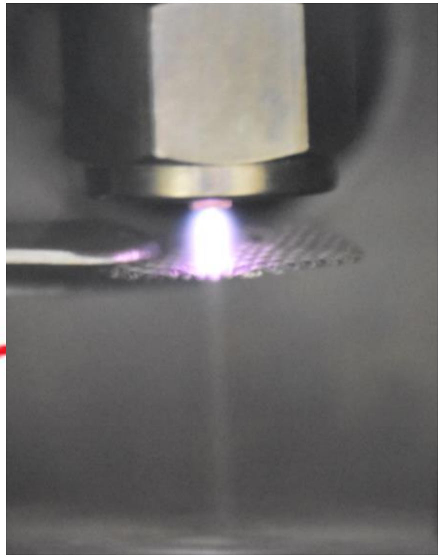
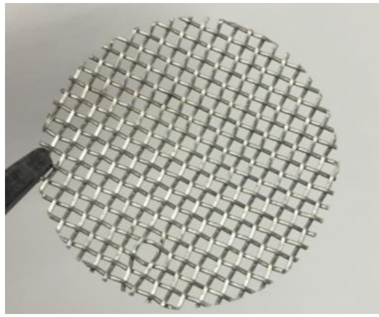
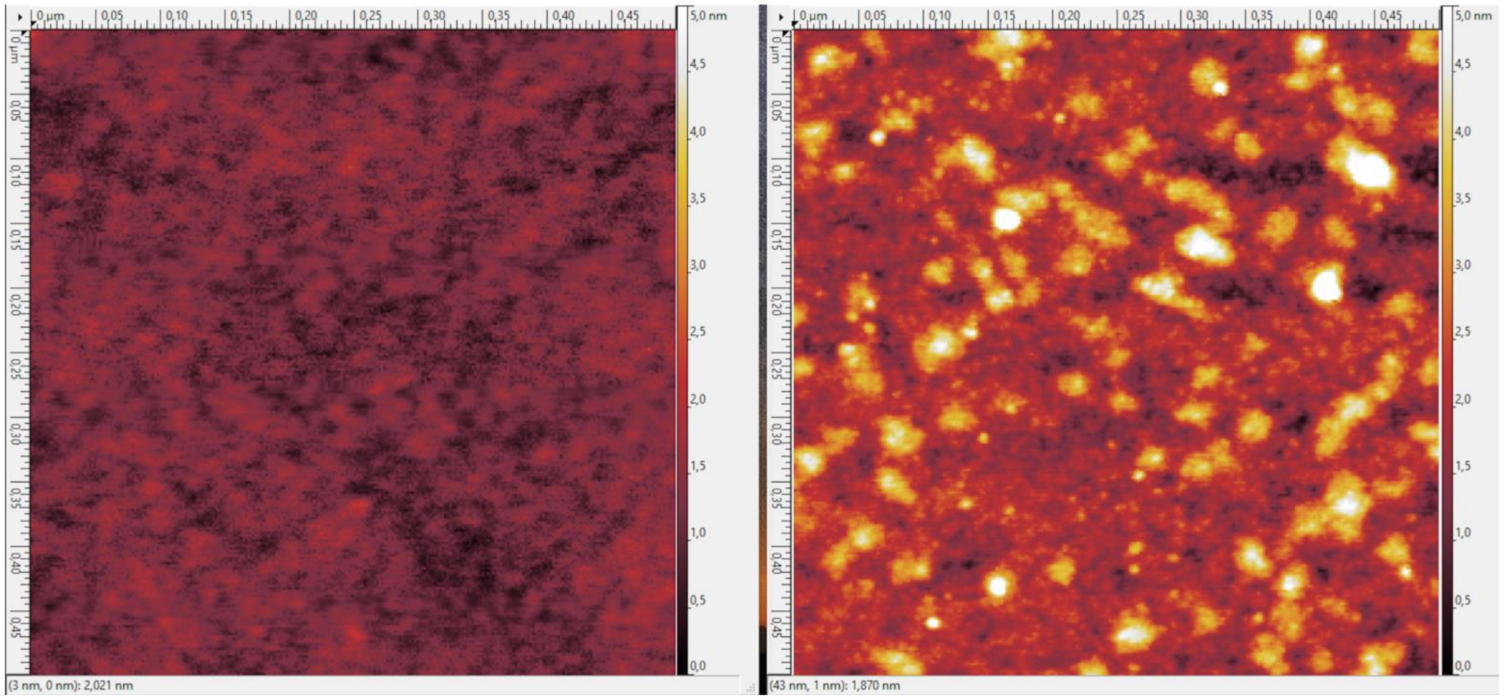






AFM Topography Image

5 nm



0 nm

Argon Plasma **NO** Precursor

Argon Plasma **WITH** Precursor

Substrate: Si, t = 1 min, P = 760 torr, Δ d = 10 mm

→ **Achieved Pt nanoparticles: 3-10 nm, average = 4 nm Pt**

Summary & Next Steps

- Deposited diverse range of Pt nanostructures and morphologies
- Pressure and capillary substrate distance had greatest effect on Pt morphology
- Achieved average Pt nanoparticle size of 4 nm

- PtNi Alloy synthesis → Ni is readily available, less expensive than Pt
- Is PtNi catalytically active for ORR?
- Electrocatalytic testing underway

Acknowledgements

Professor Michael Gordon

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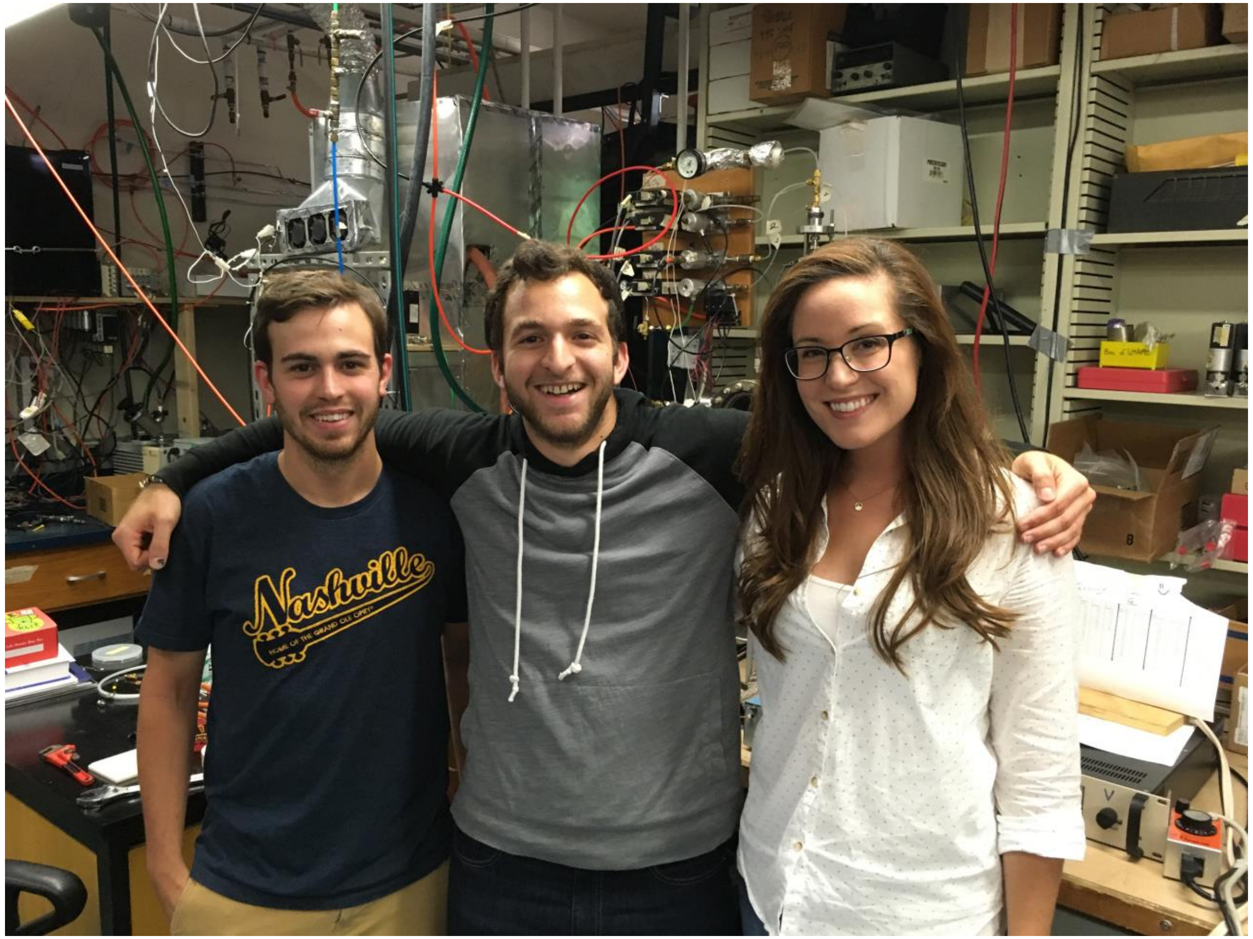
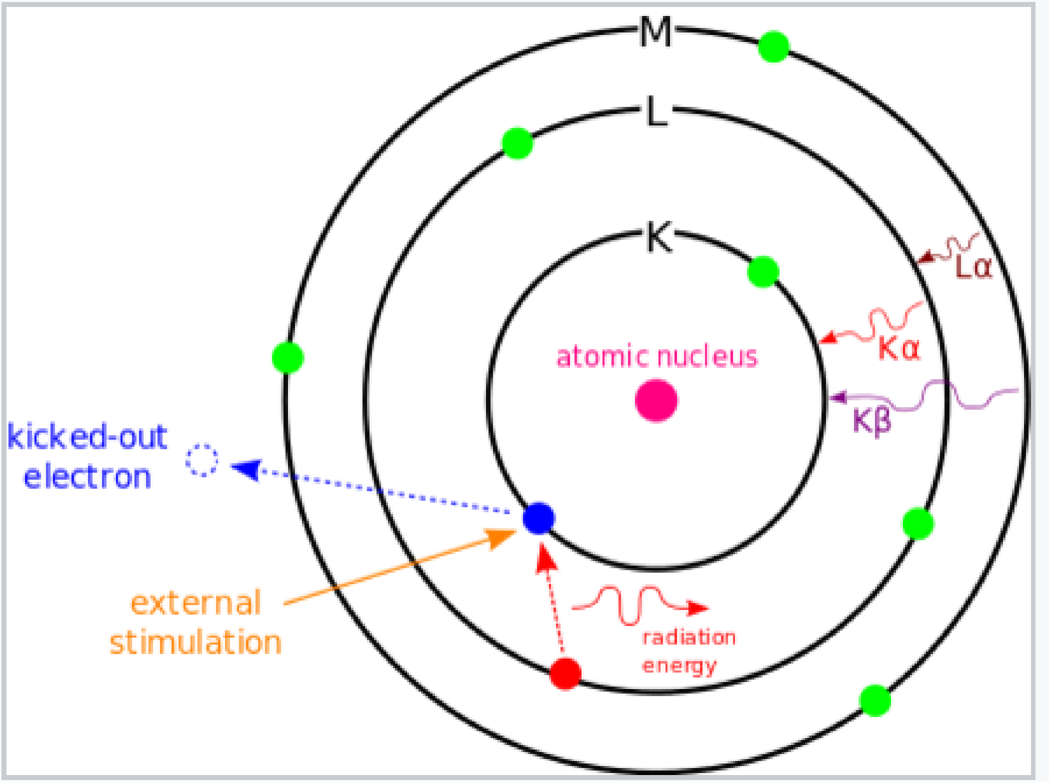
Funding

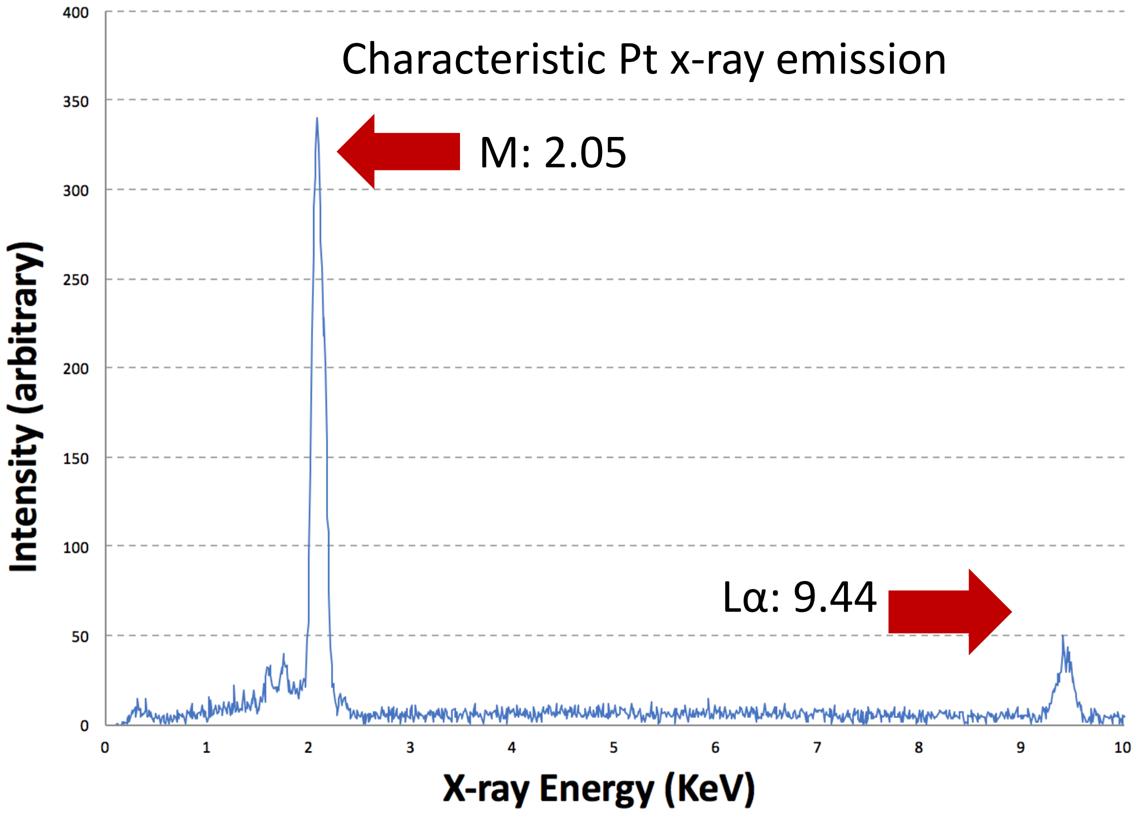


PhD Students: Joffrey Baneton and Katherine Mackie

Pt-film composition: EDX analysis

EDX = energy dispersive x-rays analysis

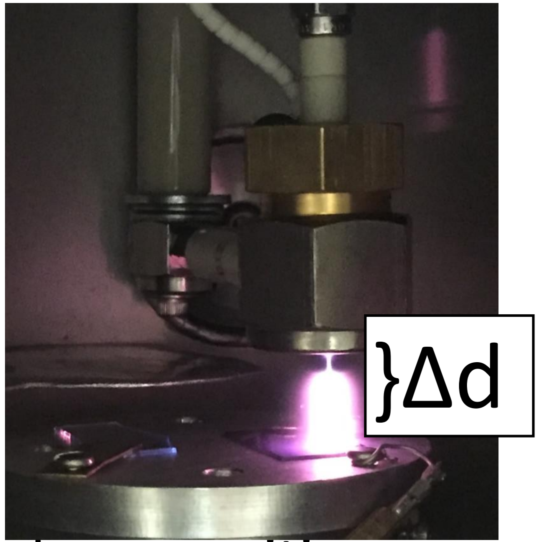




- Electron beam **kicks out core e$^-$**, outer shell e$^-$ fills, characteristic **x-ray released**
- Chemical elements present + relative abundance

Method to find Optimized Parameters for Nanoparticle Synthesis

- Design of experiments to test Pressure, O_2 addition, Pt-precursor temp. & capillary-substrate distance effects on resulting films
  - Pressure: 760 Torr
  - Deposition without 5% O_2 in plasma jet
  - Pt-precursor sublimation temperature: 40, 45 ^oC



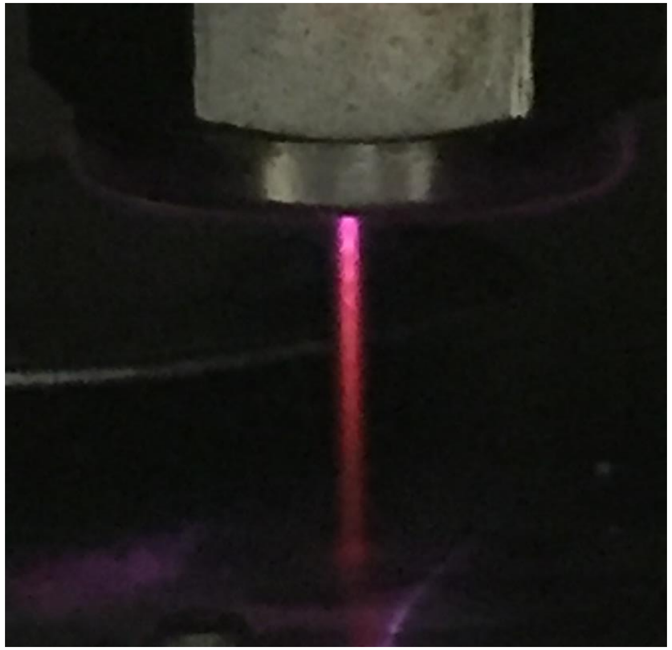
- Film characterization
  - SEM: morphology, thickness
  - EDX (energy dispersive x-ray spectroscopy): film elemental composition
  - AFM: 30 sec, 1 min deposits to examine if nanoparticles are formed

Light Emission from Microplasma

Low Pressure: $e^- + Ar^o \rightarrow Ar^*$

Red Light Emission: $Ar^* \rightarrow Ar^o$ + red

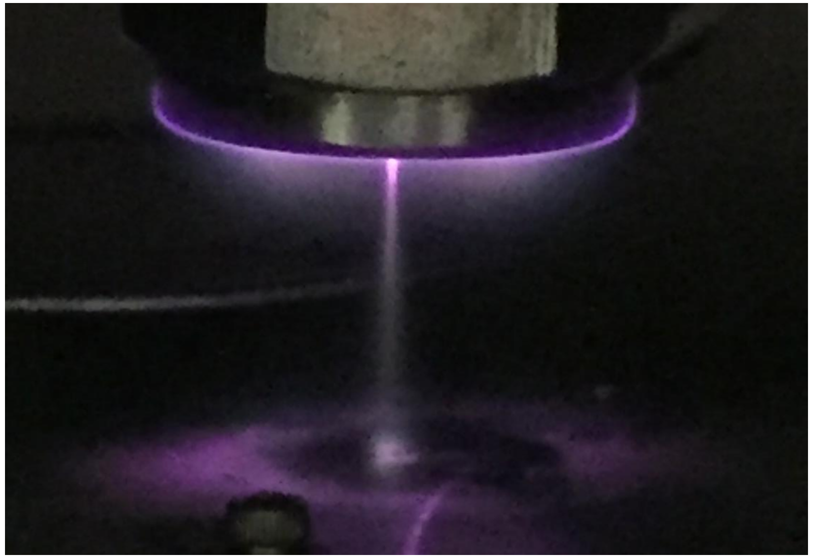
P < 50 torr



High Pressure: $e^- + Ar^o \rightarrow Ar^{+*} + e^-$

Blue Light Emission $Ar^{+*} \rightarrow Ar^+$ + blue

P > 150 torr



- **Kinetic Energy** of electron ionizes Ar to $Ar^+ + e^- \rightarrow$ **Electron cascading** → Plasma
- Excited States: $e^- + Ar^o \rightarrow Ar^*$