Imaging the Nucleation and Growth of Nanoparticles in Solution

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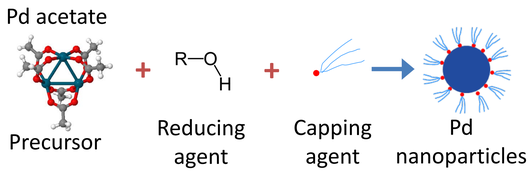
Purpose

Enable the controlled synthesis of nanomaterials of well-defined size and shape through imaging of the nucleation and growth phases using complementary in-situ X-ray and microscopy techniques.

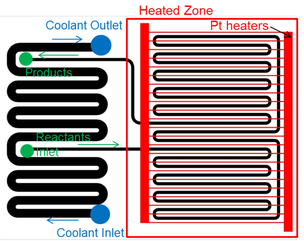
Key Successes

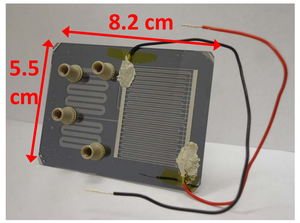
- Demonstrated millisecond-to-hour time resolution by in-situ X-ray absorption fine structure (XAFS) and small-angle X-ray scattering (SAXS) study in microfluidic reactor
- Showed that nucleation burst is not required for synthesis of small, monodisperse nanoparticles:
  - Metal/capping agent interaction leads to self-limiting autocatalytic growth through surface poisoning
  - Size is manipulated by the binding strength of metal/capping agent
- In-situ environmental transmission electron microscopy (ETEM) revealed that Ostwald ripening is main growth mechanism of carbon-supported Pd nanoparticles.

Approach

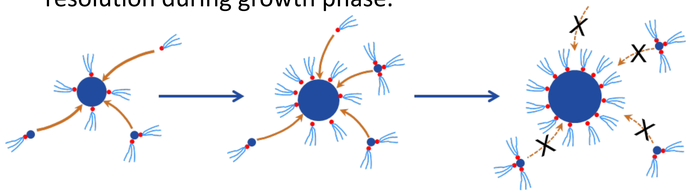


A look from the inside: elucidating synthesis mechanisms using microfluidic multi-modal characterization



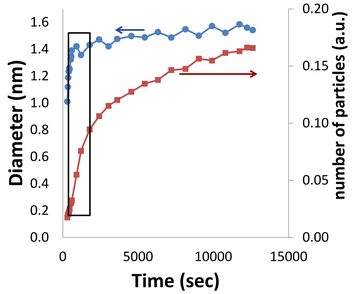


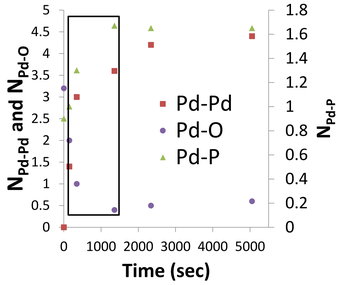
- Novel microfluidic reactor for synchrotron beamline in-situ XAFS and SAXS studies of nanoparticles synthesis in solution.
- X-ray window allows millisecond time resolution during nucleation and up to minutes in time resolution during growth phase.



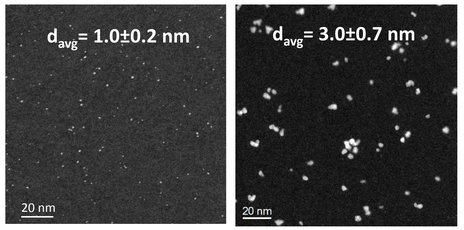
Research Accomplishments

Pd nanoparticle synthesis mechanisms in solution





- In-situ SAXS (left) showed continuous increase in number of particles indicating slow nucleation. Fast growth in the early times suggests autocatalytic reduction of the precursor.
- In-situ XAFS (right) showed increase in the Pd-P coordination number indicating an increased coordination of Pd with capping agent trioctylphosphine (TOP). The black boxes highlight the time period where coordination with TOP increased and growth rate dropped.

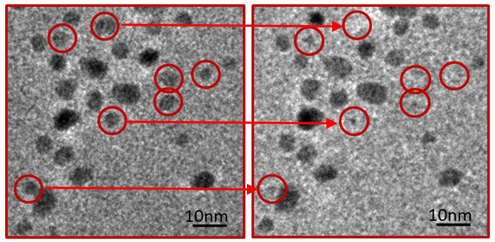


STEM images showing the effect of capping agent on the size of Pd nanoparticles. Trioctylphosphine (strong binding ligand, left) vs. oleylamine (weaker ligand, right).

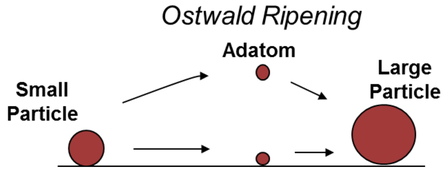
Proposed model: Increased coordination of capping agent with precursor and nanoparticle surface leads to observed arrested growth at a size determined by binding strength of capping agent with nanoparticle surface.

Karim AM et al. 2014. *JACS*, submitted; Karim AM et al. 2014. *Small*, in preparation

Pd nanoparticle sintering mechanisms



- In-situ ETEM study at 500° C shows growth of some particles (middle, 2 min), while others are shrinking/disappearing (right, 20 min).
- No particle migration was observed (right, 20 min) suggesting that Ostwald ripening is the main sintering mechanism.



Sintering mechanism for Pd/C at 500 °C in vacuum

Benavidez AD et al. 2012. *ACS Catalysis* 2:2349

Next Steps

- Tools will be available for projects in Materials Synthesis across Scales (MS3) initiative
- Proposal being developed for DOE-BES.