Study of Capped Metallic Nanoparticles with Infrared Spectroscopy

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Goals

• Observe the unique infrared spectrum of the organic-capped metallic nanoparticles

• Determine the correlation between organics and the IR spectra of the particles

• Investigate the best method for producing a uniform thin film
Importance

• Variable properties due to size, shape and organic capping agents.

• High value in catalysis, biomedicine

• Gold and platinum expensive; copper possible alternative?

http://www.nanopaprika.eu/photo/laser-generated-metal-1
Nanoparticle Synthesis

- Synthesized with organics
- Keeps metals from oxidizing
- Morphology not always spherical

(a) One-step route for synthesis of bimetallic or tri-metallic nanoparticles,
(b) Loading on support materials and activation treatment.
FTIR Spectroscopy

• Interferogram \(\rightarrow\) IR spectrum \(\rightleftharpoons\) Fourier Transform
• Using continuous scan interferometry: moving mirror in continuous motion.
• Mid IR range \(\rightarrow\) 4000cm\(^{-1}\) to 400cm\(^{-1}\), or 2.5-25 microns
Initial Steps

• Silicon substrate
• Drop-cast method of deposition – knowingly not uniform
• What peaks are most prominent? For what samples?
• Tetraoctylammonium bromide (TOABr) present in most toluene solutions
• Design a fixture for samples
TOABr spectrum

- Methyl symmetric / methylene asymmetric C-H stretching: ~2900 to 2800 cm⁻¹
- Methyl asymmetric C-H bending or methylene scissoring: ~1460 cm⁻¹
- Methylene rocking: ~723 cm⁻¹
Narrowing Focus

• Several different metallic samples with different properties
• Copper solutions
  – More visible, and prominent IR peaks
  – Smaller particle size and presence of TOABr

Transmission Electron Microscopy (TEM) image of Cu NPs 5-7nm in diameter

http://www.ssnano.com/inc/sdetail/370
Cu with TOABr sample compared to TOABr spectrum

Cu with TOABr sample

TOABr sample

Maybe Something there as well

TOABr

TOABr
Cu -- effect of added quantity

6 drops, in the center of the drop area
6 drops, on green ring - higher concentration

As the concentration increases...

Deeper
broader
Deeper
deeper
Manipulating Properties

• Capped with dodecanethiol.

• Heating the Cu samples-Copper sulfide nanocrystals?

• Limited to <125°C-TOABr blocked IR light above temperature

• Created a different spectrum

• How can heating be used to control the behavior of the particles?

http://pubs.acs.org/doi/pdfplus/10.1021/cm903038w
Cu before and after heating at ~125°C for 1 hour

Annealed sample

Cu with TOABr sample, no manipulation

Possibility that this is TOABr related– don’t know how it behaves under higher temperatures.
TOABr before and after heating, 120°C, 30 minutes

Heated TOABr sample

Looks familiar

Nothing unusual…
Cu with TOABr with TOABr - both heat treated

TOABr annealed

Cu with TOABr annealed

![Graph of wavenumbers (cm⁻¹) vs. Signal/Beam, with peaks and annotations indicating TOABr and ???]
Analysis

• Unusual peaks formed

• Different possible causes
  – Copper sulfide compounds? Different formulas.
  – Nanocrystals vs nanodisks vs nanospheres...
  – TOABr and capping agent reacting?
  – Just the Copper?

• FTIR can be used to identify properties unique to the nanoparticles/capping agents
Plasma Etching to Remove Organics

- Etched for 70 seconds
- Only Cu had visible change
  - Caused by heating?
- Didn't remove all organics
- Longer time or thinner sample?

Initial Cu sample

After 30 seconds

After 70 seconds
Cu with TOABr before and after etching for 70 seconds

Sample after 70 seconds of etching
Sample before etching

Could the strange change be just a shift? Is it something new entirely?
Graph of Cu with TOABr etched vs annealed

Etched sample

Annealed sample

Could this be shifting?
Spin-Casting

- Very uniform film
- Easy to control distribution
- Very thin, possible too thin for FTIR analysis.
- Applicable to industry

Atomic Force Microscopy (AFM) of AuCu NPs spun-coated at 2000 rpm. Max thickness is <800nm. Some samples between 500-200nm.

Spinner— not the same model I used

Spin coating vs Drop-casting for Cu with TOABr sample

Spin coating- 2 layers
Spin coating- 1 layer
Drop cast- 1 drop

Distinct Curves are not present in the spin coating samples
Microcontact Printing

- Stamping nanoparticles onto substrate using polymer stamp
- Uneven distribution
- Optimum conditions?
- Needs a perfected technique
- Good with solutions with less organics (Pt, Au – hexane solutions)
- Good for larger particle size
Pt$_{45}$V$_{18}$Co$_{37}$ Stamped, 3 drops vs drop-casting and after annealing

Drop cast, 3 drops, 100X magnification

Microcontact printing, 3 drops, 100X magnification

Microcontact printing sample after annealing at 400°C for 15 minutes

AFM of annealed sample
Thickness = ~200nm.
Pt$_{45}$V$_{18}$Co$_{37}$ Drop cast vs stamping

Stamped, 3 drops
Drop cast, 3 drops

More prominent
deeper
Could be mistaken for noise

More particles on the stamped samples!
Pt$_{44}$Ni$_{14}$Co$_{42}$ before and after annealing

Stamped, before annealing

Stamped, after annealing at 400°C for 20 minutes

Next steps: TEM or AFM to get thickness and a closer image?
Pt$_{44}$Ni$_{14}$Co$_{42}$, stamped and annealed

Stamped sample

Stamped and annealed

No more C-H!

Could these be related to metal nanoparticles?

Annealing removed a lot of organics.
Conclusion

• FTIR can be used to identify capping agents used in synthesis of metallic nanoparticles
• Spin-casting method works well with high concentrations and small diameters
• Micro-contact printing works well with larger diameters and lower concentrations
• Heat activation to remove organics effective with some metallic nanoparticles
Future Work

• XRD on annealed samples to observe change in structure
• Experiment with spin-casting.
• More powerful etching?
• Microcontact printing-mastering the technique
• Comparison with nanoparticle samples with different sizes or capping agents?
Thank you