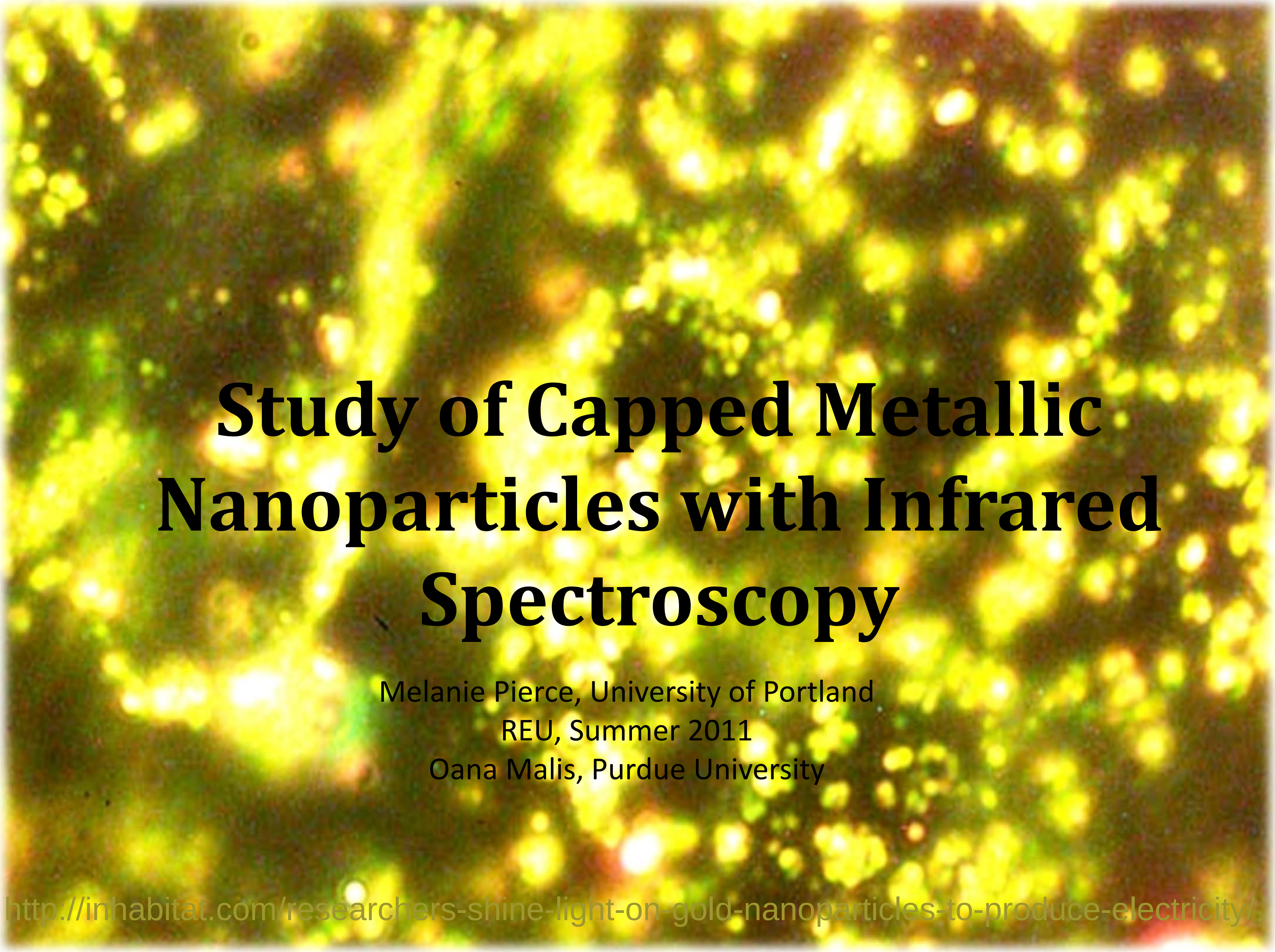


Study of Capped Metallic Nanoparticles with Infrared Spectroscopy

Melanie Pierce, University of Portland
REU, Summer 2011
Oana Malis, Purdue University

http://inhabitat.com/researchers-shine-light-on-gold-nanoparticles-to-produce-electricity/

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

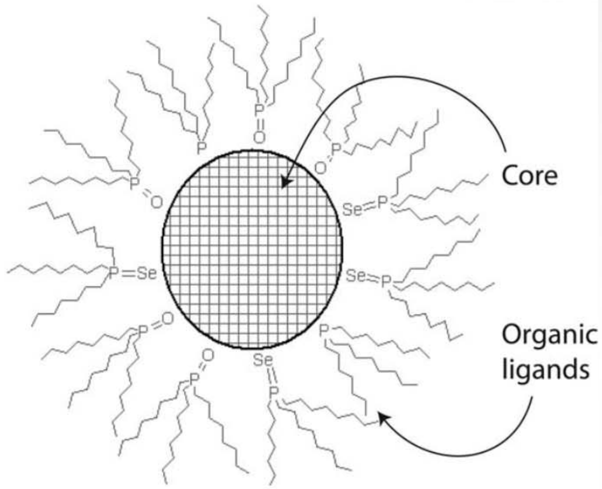
Importance

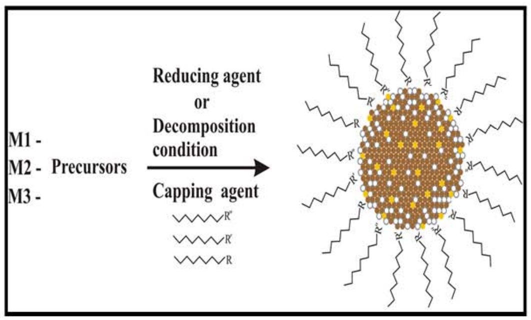
- Variable properties due to size, shape and organic capping agents.
- High value in catalysis, biomedicine
- Gold and platinum expensive; copper possible alternative?

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

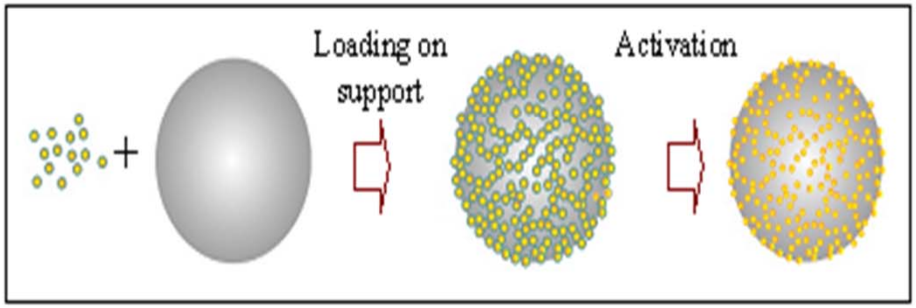
Nanoparticle Synthesis

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





(a)

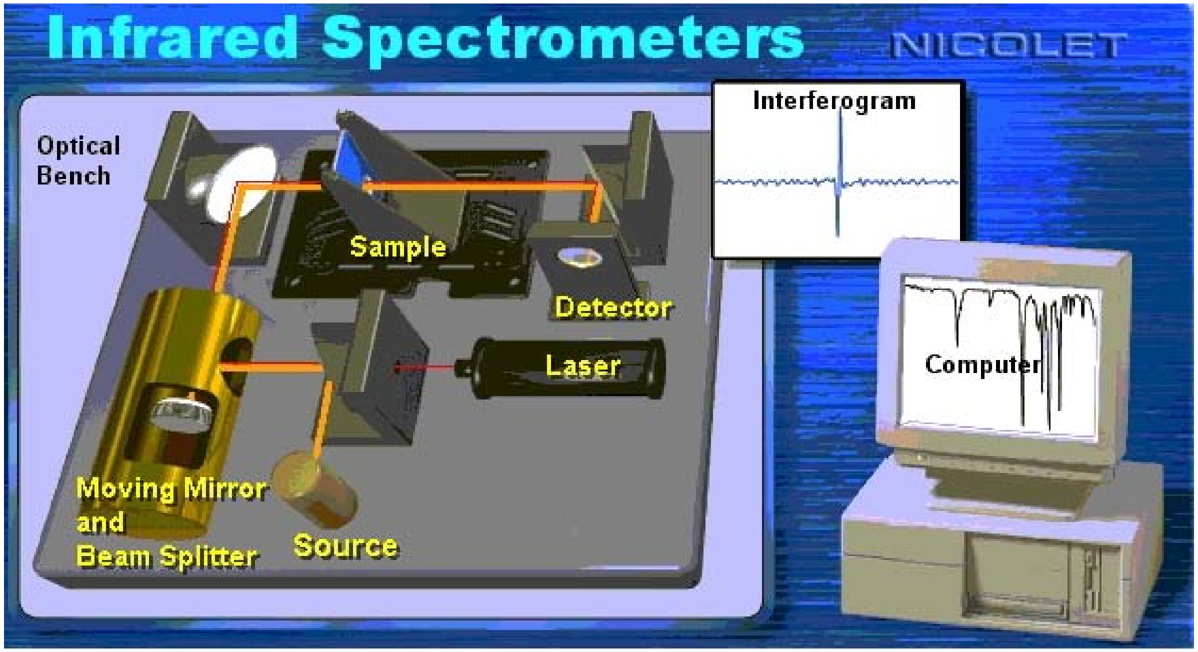


(b)

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

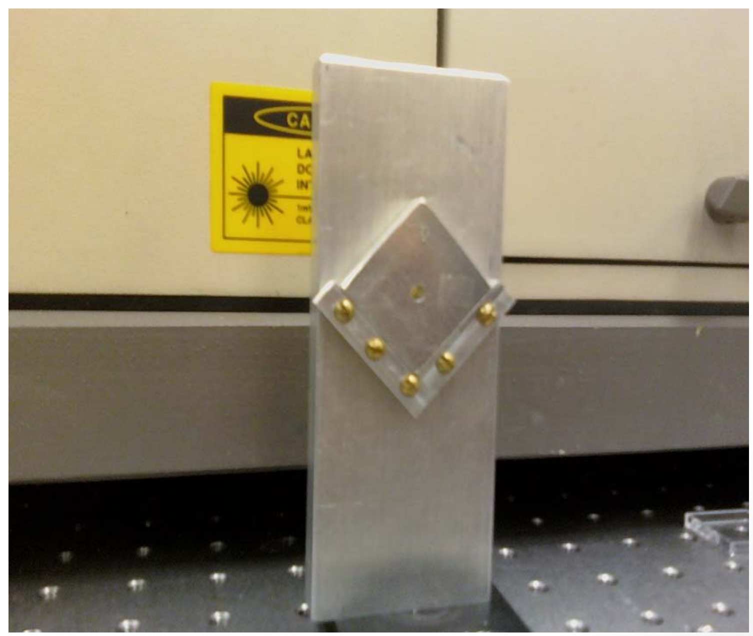
FTIR Spectroscopy

- Interferogram -> IR spectrum ═ Fourier Transform
- Using continuous scan interferometry: moving mirror in continuous motion.
- Mid IR range → 4000cm^-1 to 400cm^-1, or 2.5-25 microns

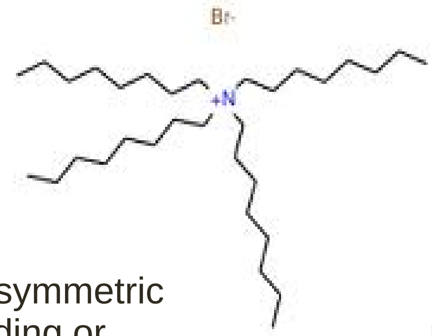


Initial Steps

- 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



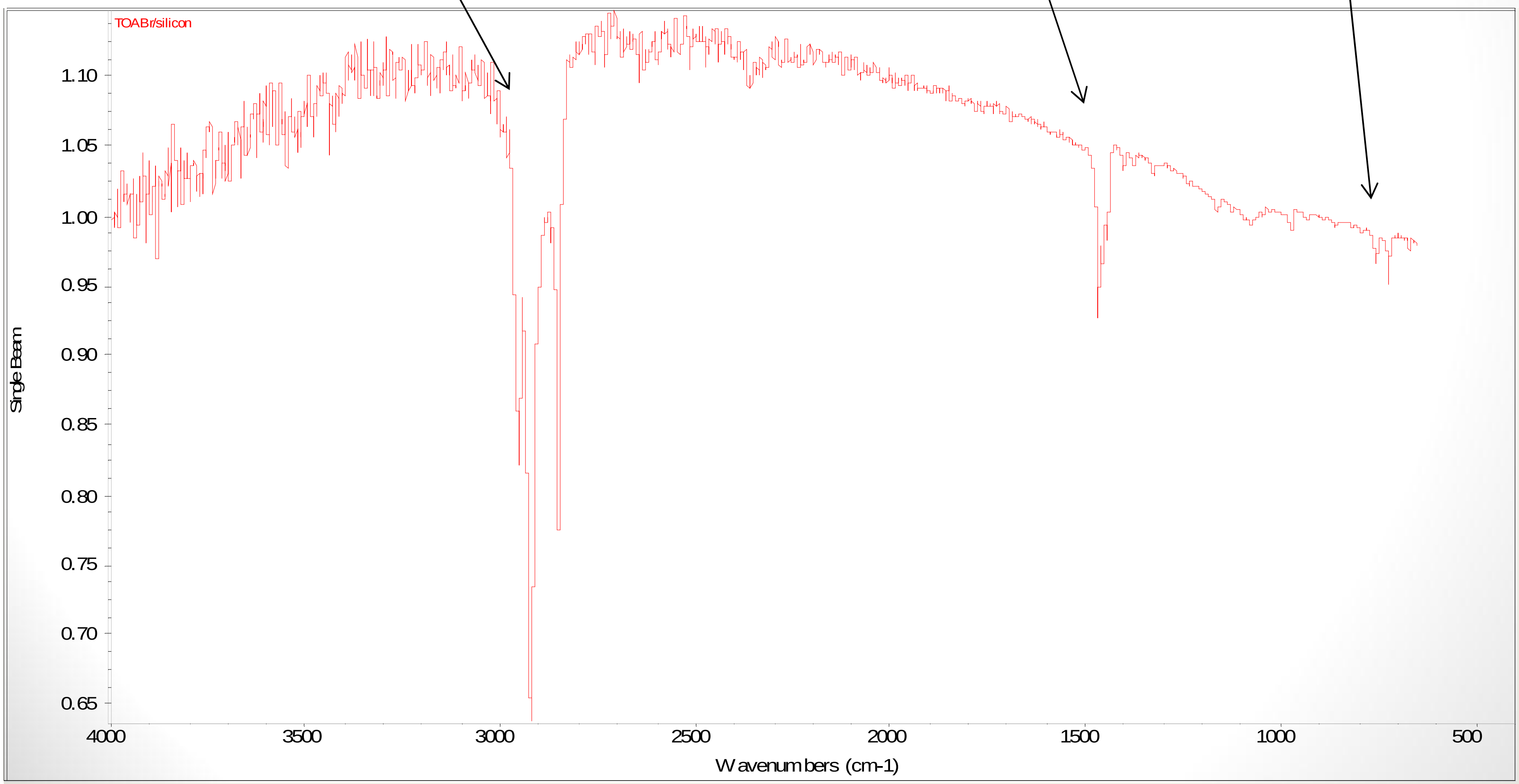
TOABr spectrum



methyl symmetric /methylene asymmetric C-H stretching ~2900 to 2800cm-1

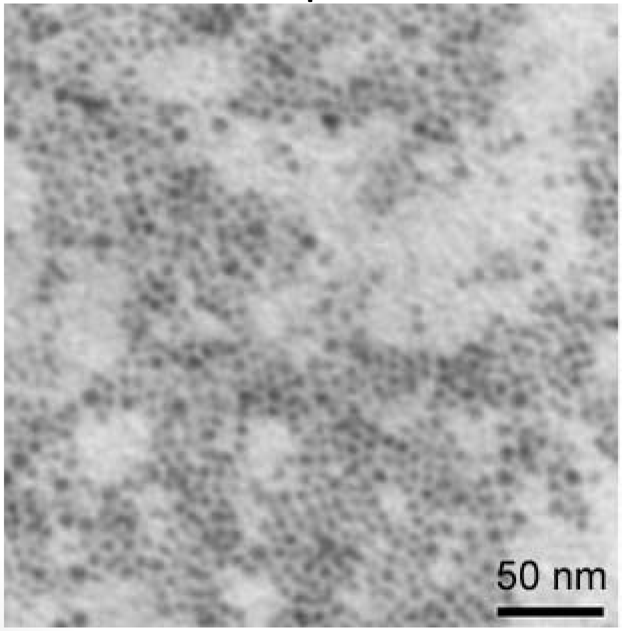
methyl asymmetric C-H bending or methylene scissoring ~1460cm-1

Methylene rocking ~ 723cm-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



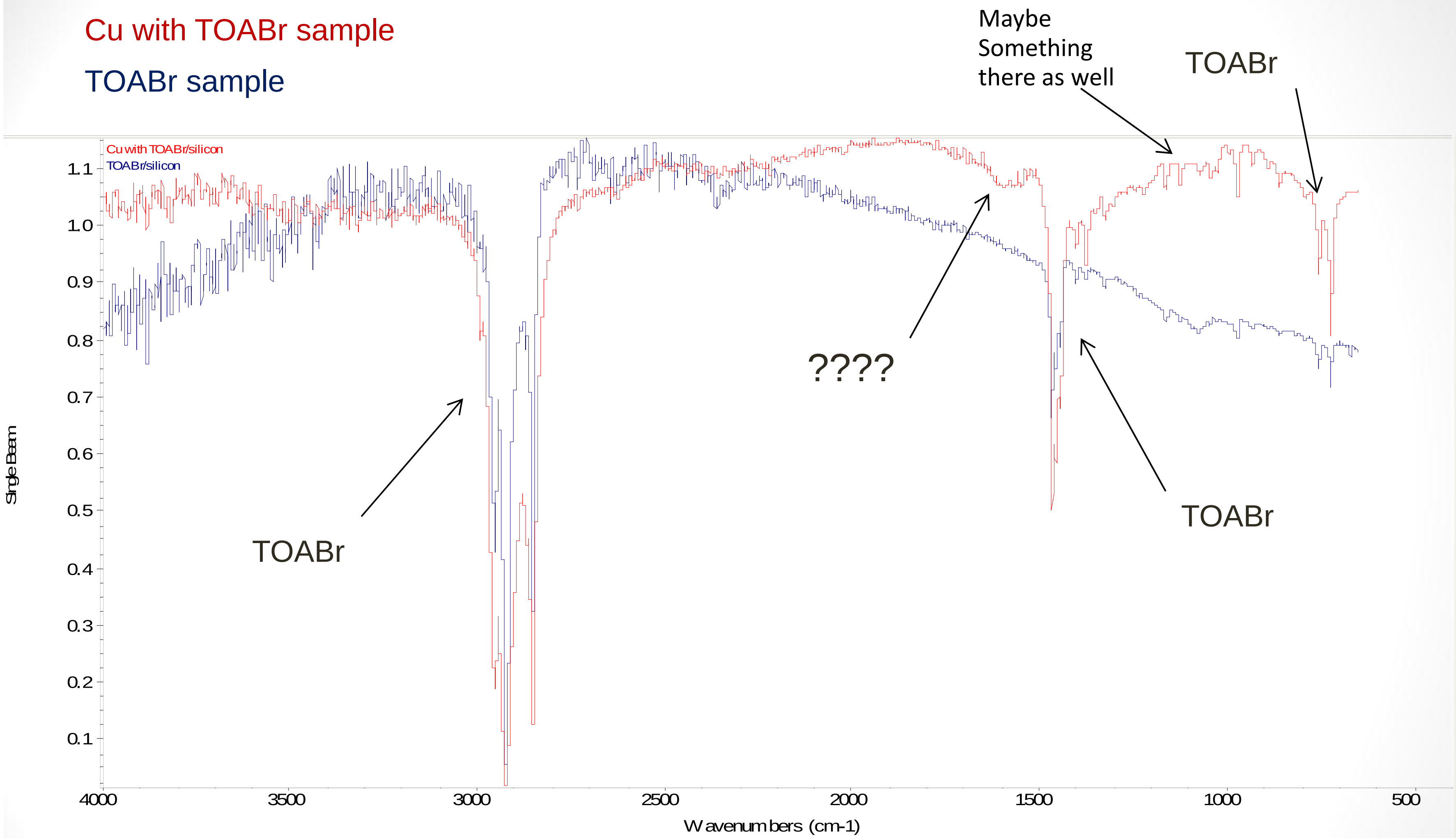
Transmission Electron Microscopy (TEM) image of Cu NPs 5-7nm in diameter

http://www.ssnano.com/inc/sdetail/370

Cu with TOABr sample compared to TOABr spectrum

Cu with TOABr sample

TOABr sample

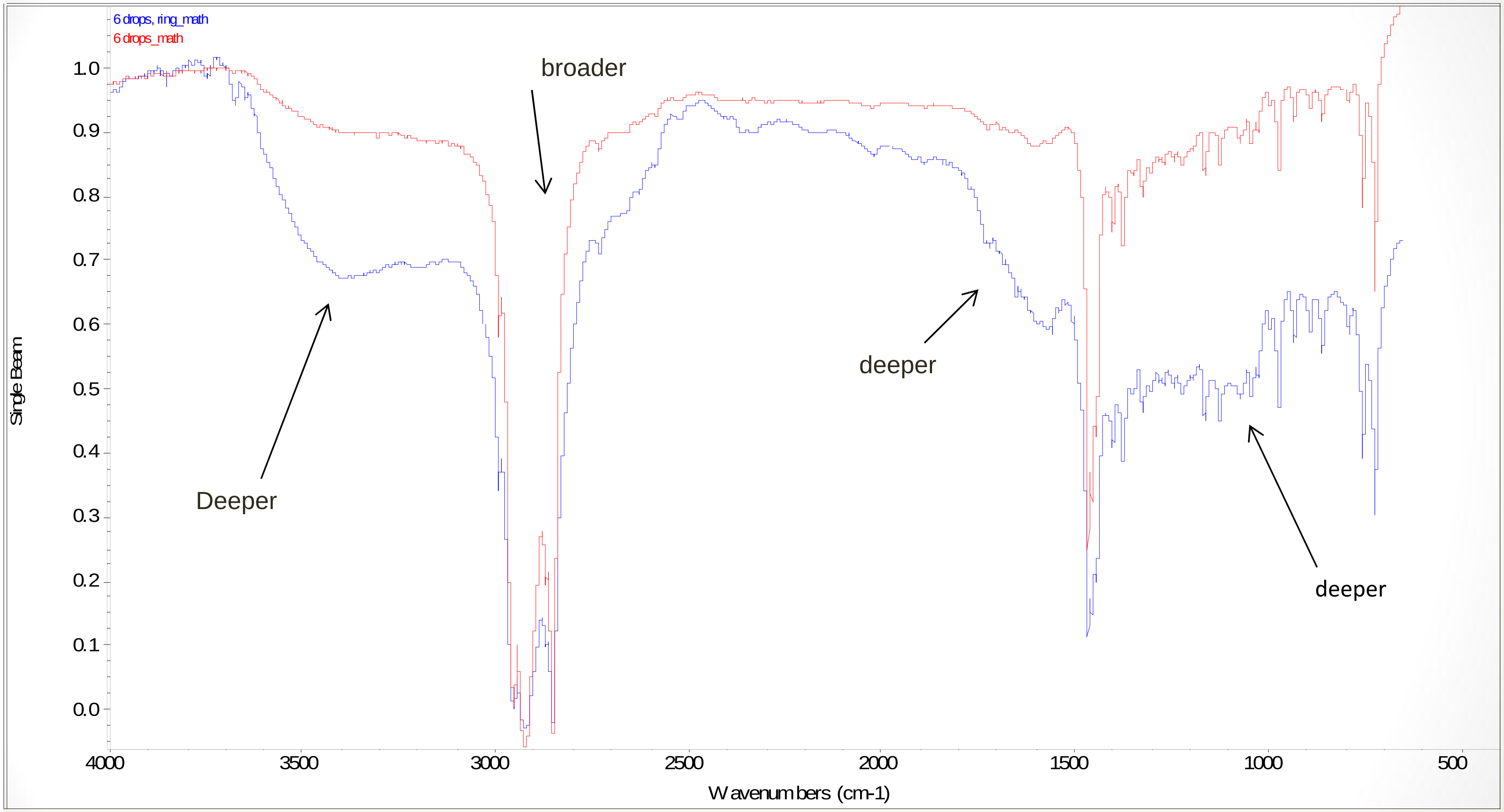


Cu -- effect of added quantity

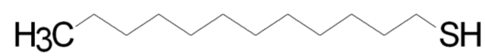
6 drops, in the center of the drop area

6 drops, on green ring- higher concentration

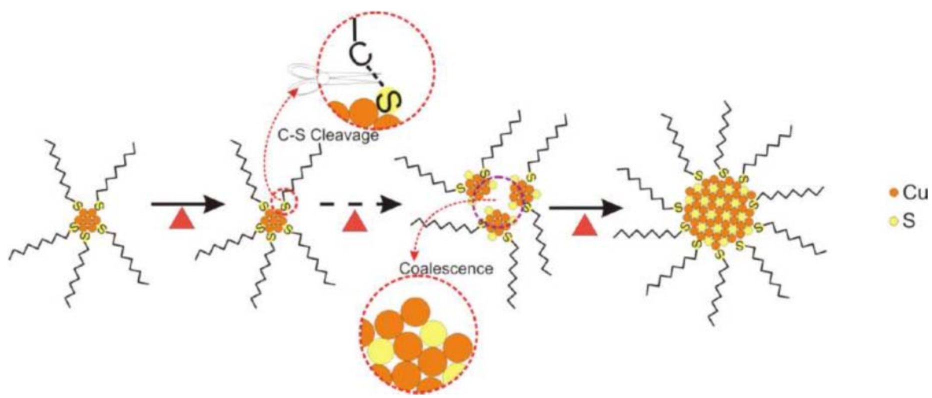
As the concentration increases…



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?

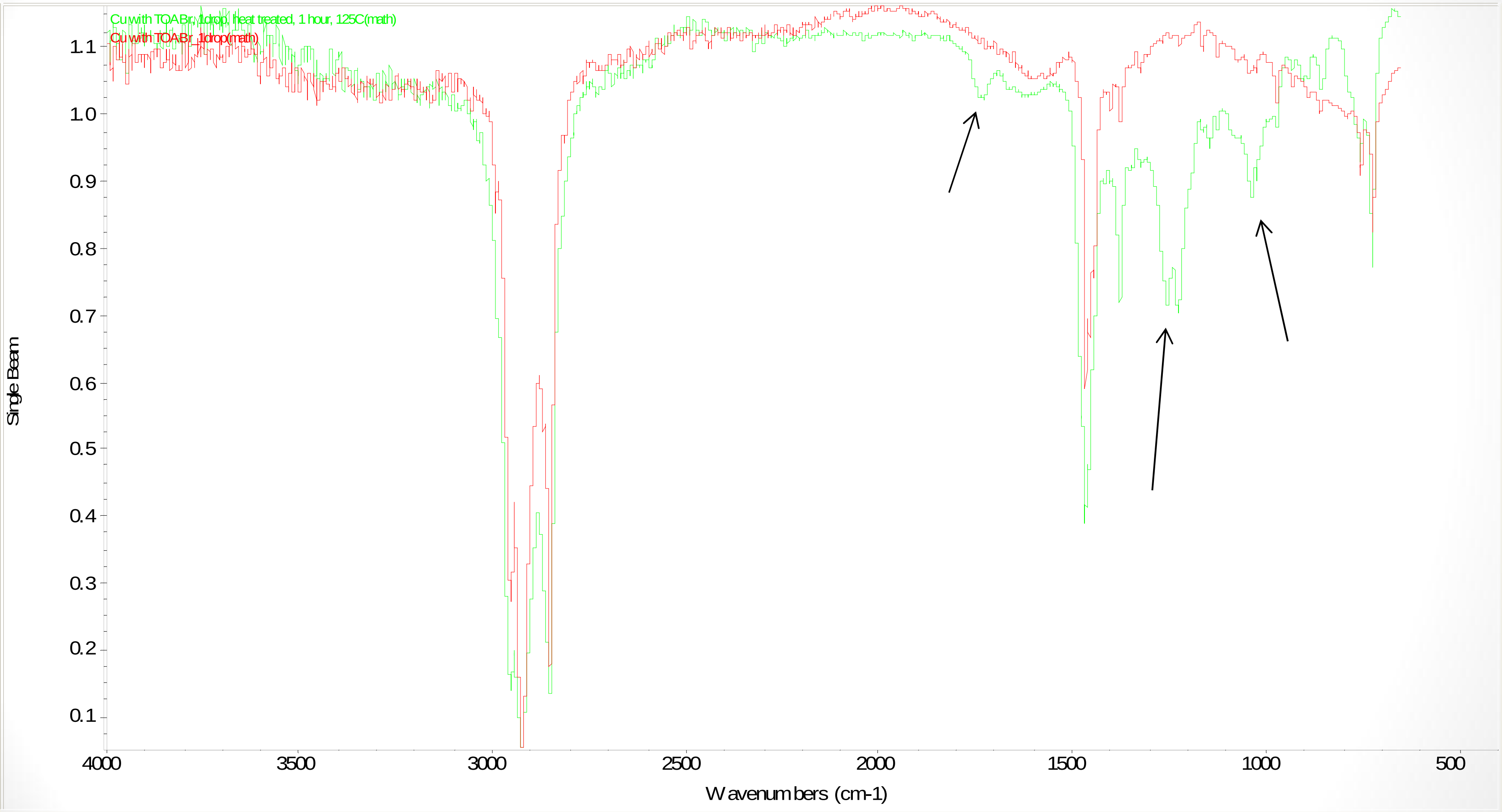


http://pubs.acs.org/doi/pdfplus/10.1021/cm903038w

Cu before and after heating at ~125˚C for 1 hour

Annealed sample

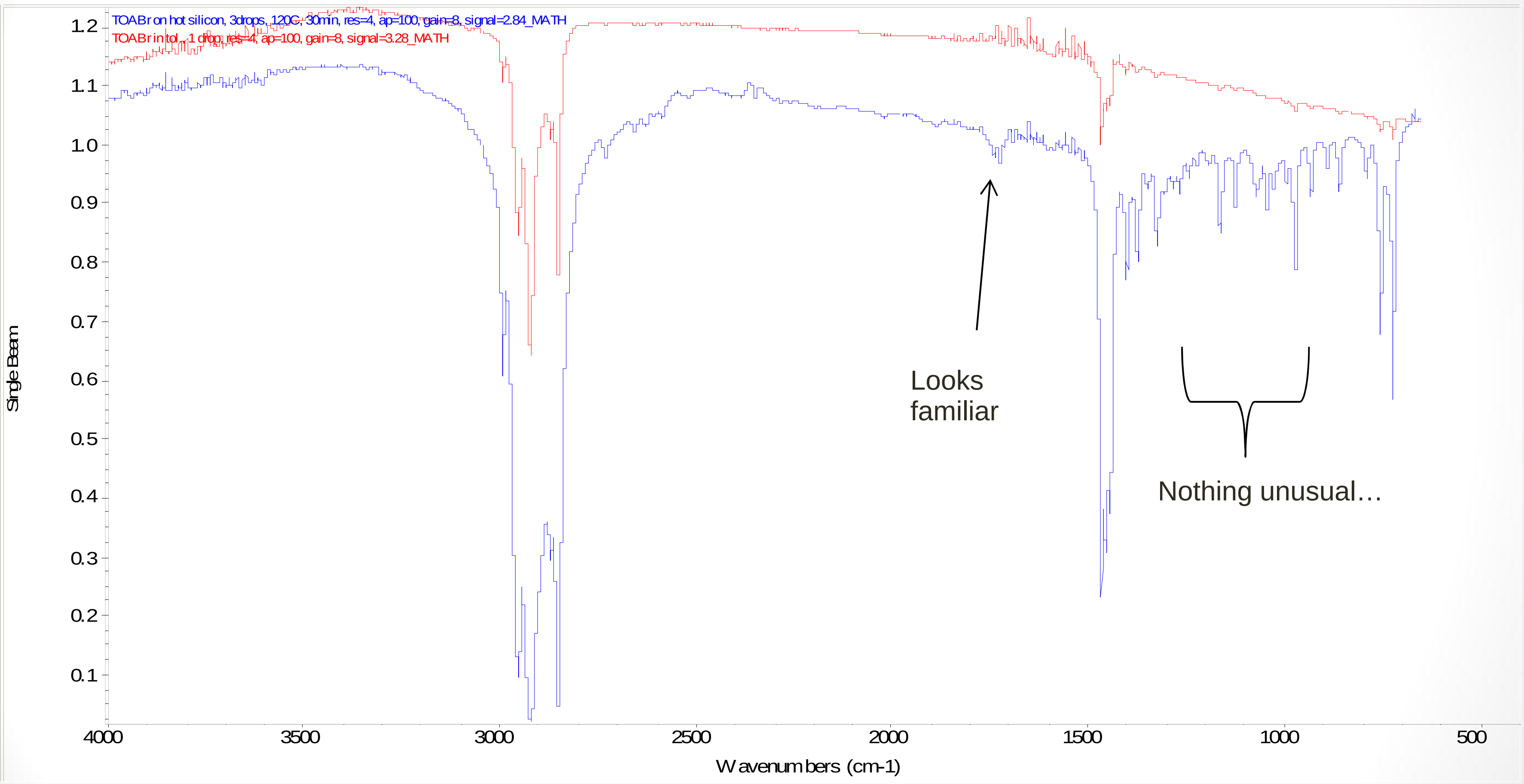
Cu with TOABr sample, no manipulation



Possibility that this is TOABr related– don't know how it behaves under higher temperatures.

TOABr before and after heating, 120˚C, 30 minutes

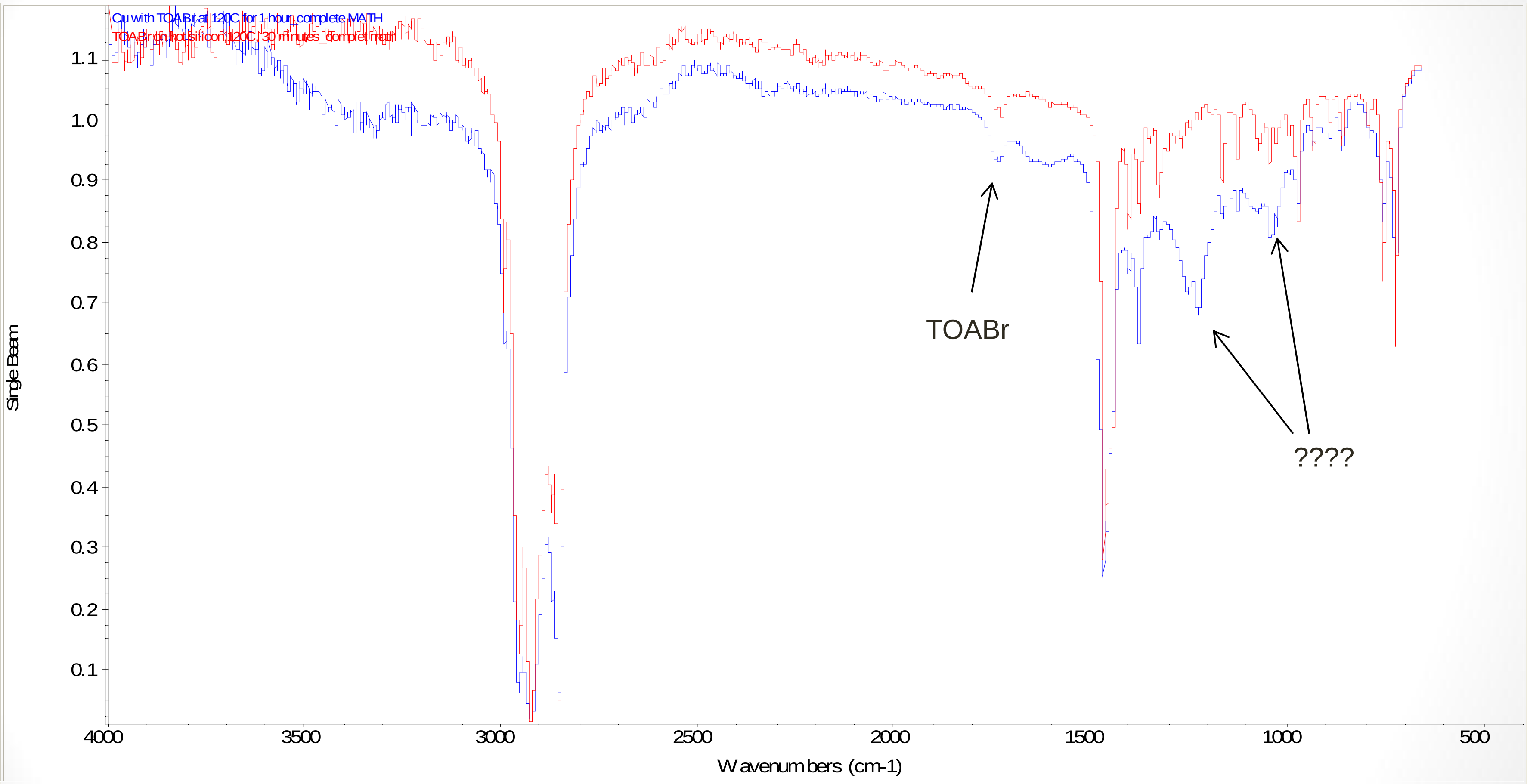
Heated TOABr sample



Cu with TOABr with TOABr- both heat treated

TOABr annealed

Cu with TOABr annealed

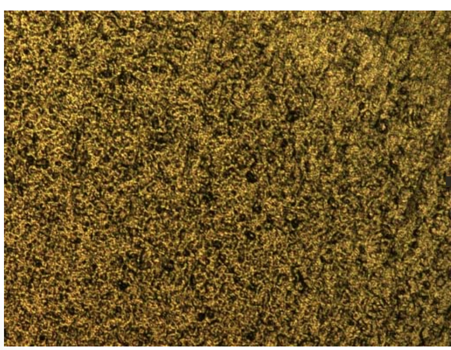


Analysis

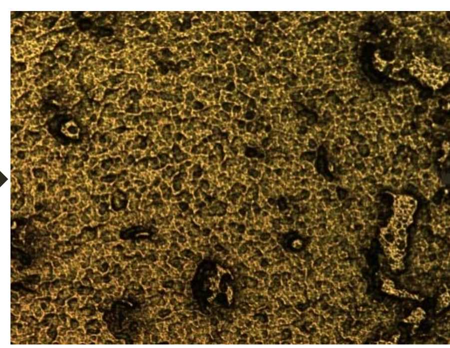
- Unusual peaks formed
- Different possible causes
  - Copper sulfide compounds? Different formulas.
  - Nanocrystals vs nanodisks vs nanospheres…
  - TOABr and capping agent reacting?
  - Just the Copper?
- FTIR can be used to identify properties unique to the nanoparticles/capping agents

Plasma Etching to Remove Organics

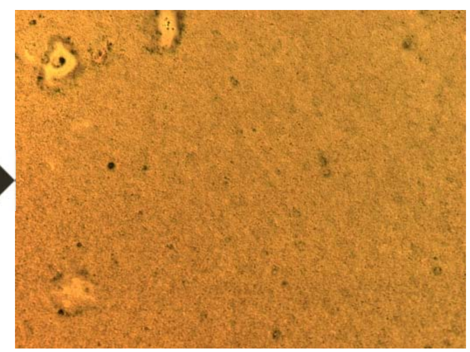
- Etched for 70 seconds
- Only Cu had visible change
    - Caused by heating?
- Didn't remove all organics
- Longer time or thinner sample?



Initial Cu sample



After 30 seconds



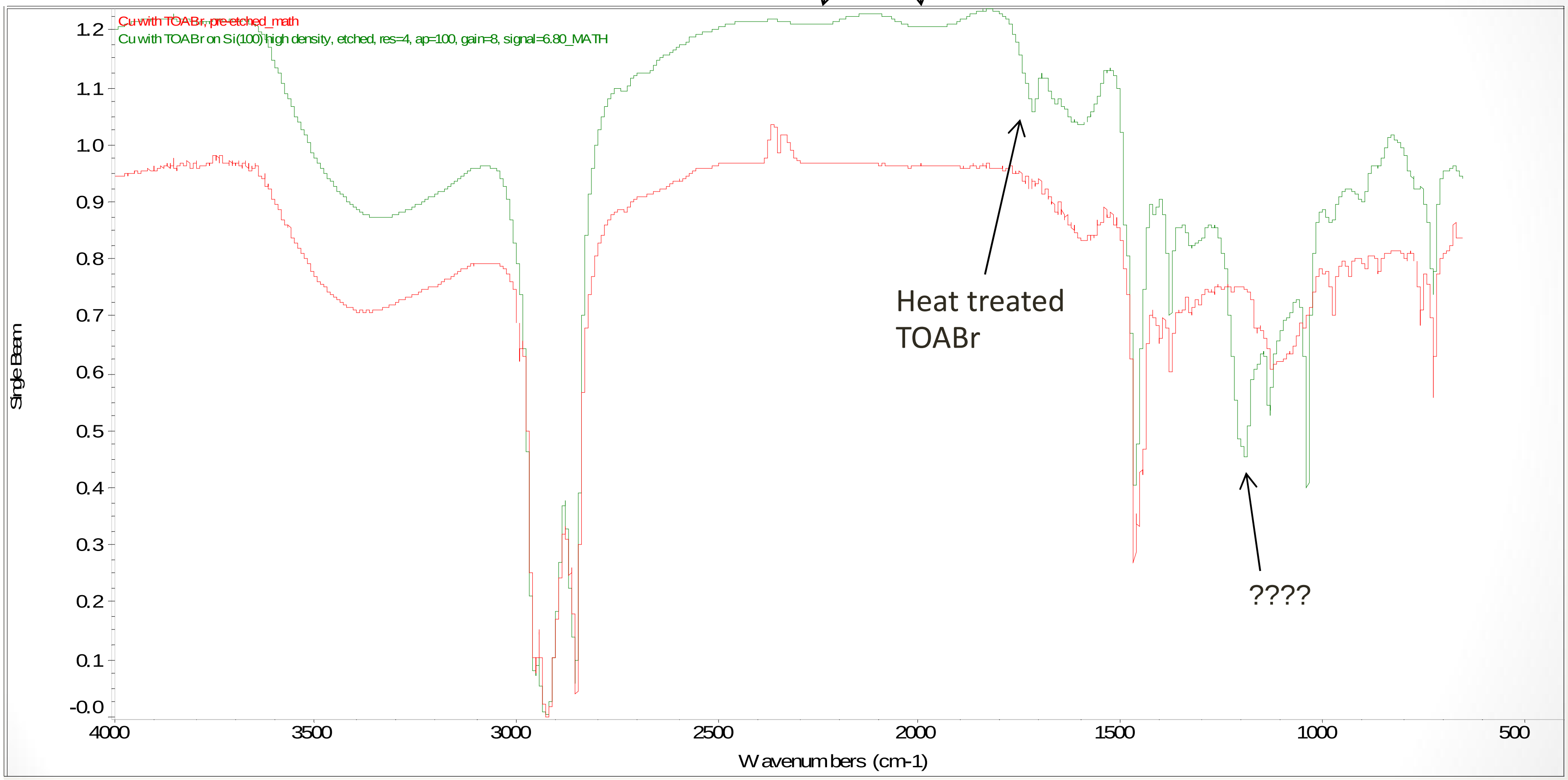
After 70 seconds

Cu with TOABr before and after etching for 70 seconds

Sample after 70 seconds of etching

Sample before etching

New peaks?

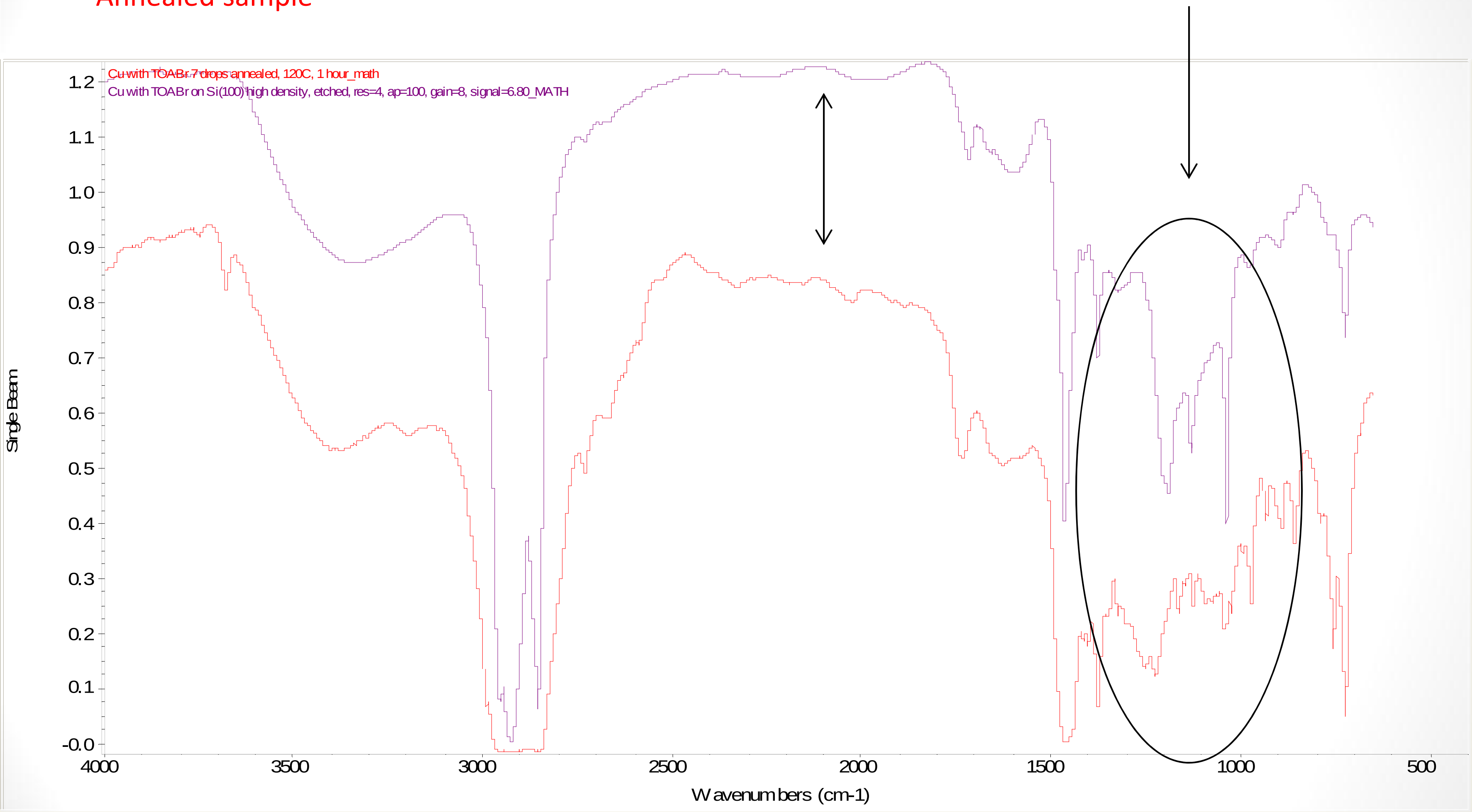


Could the strange change be just a shift? Is it something new entirely?

Graph of Cu with TOABr etched vs annealed

Etched sample

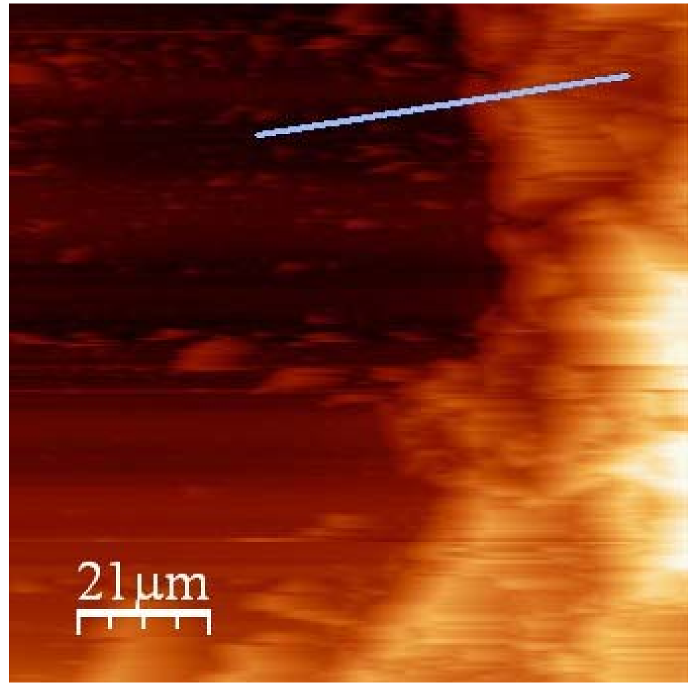
Annealed sample



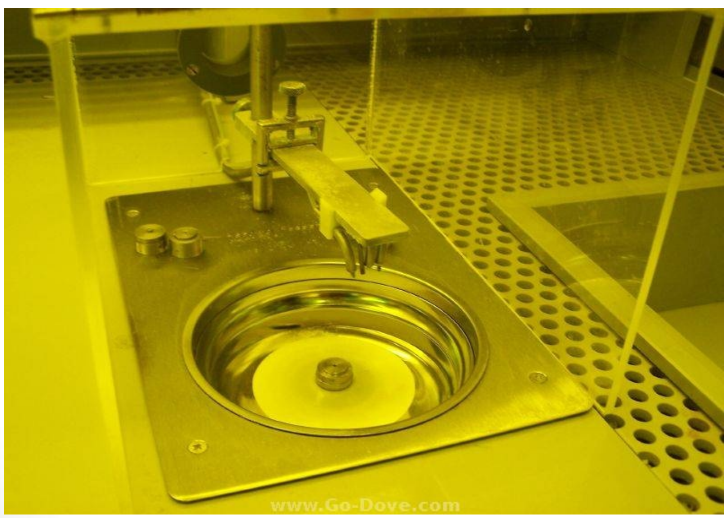
Could this be shifting?

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

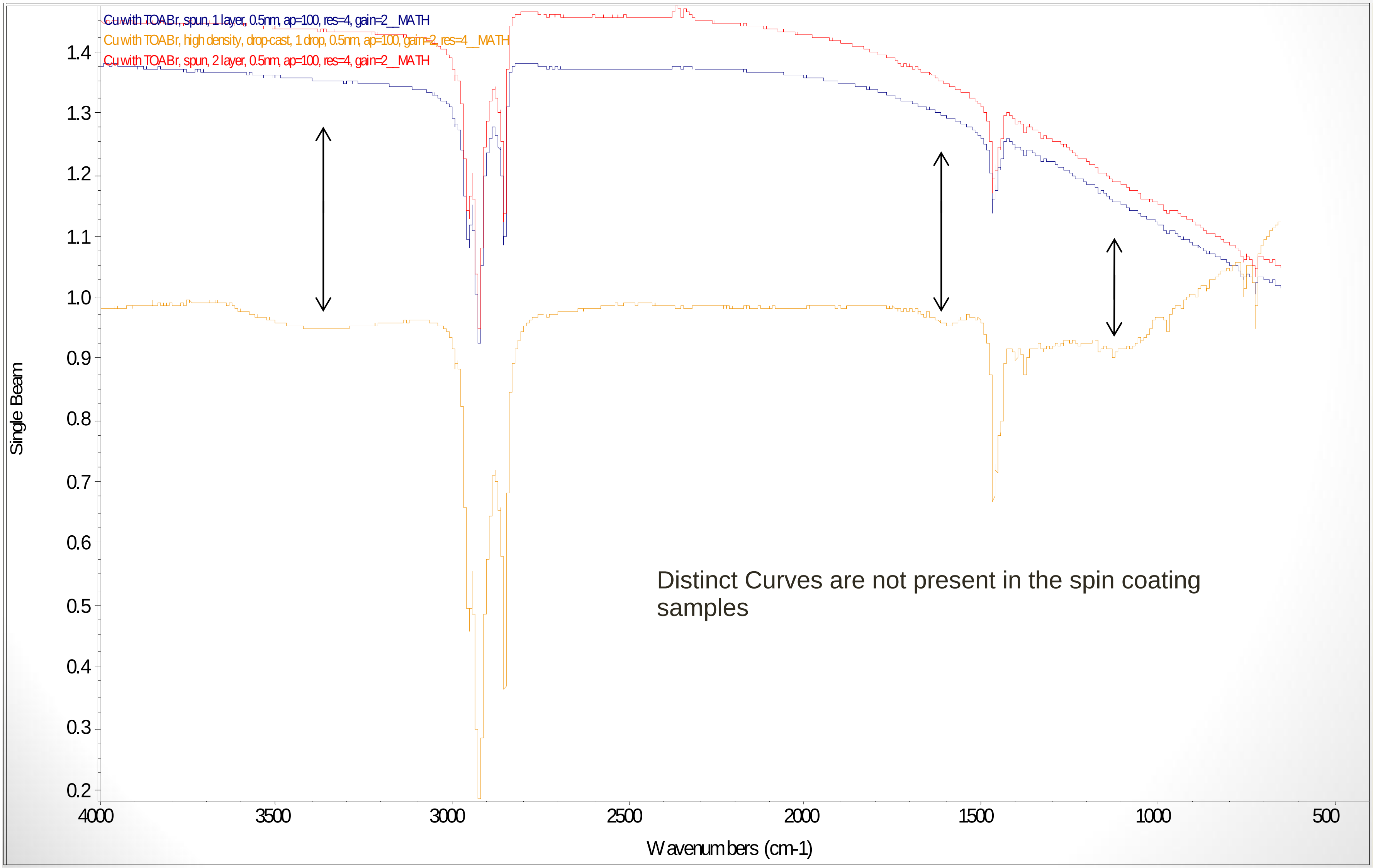
https://www.go-dove.com/event-14642/AL-Technologies-Epiwafers-Optical-Electronics/lot-72/HEADWAY-RESEARCH-O101D-R485-Resist-Spinner-with-Dispensing-System-Heat

Spin coating vs Drop-casting for Cu with TOABr sample

Spin coating- 2 layers

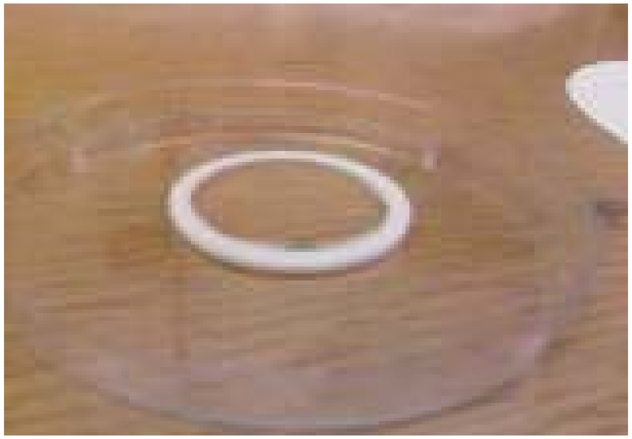
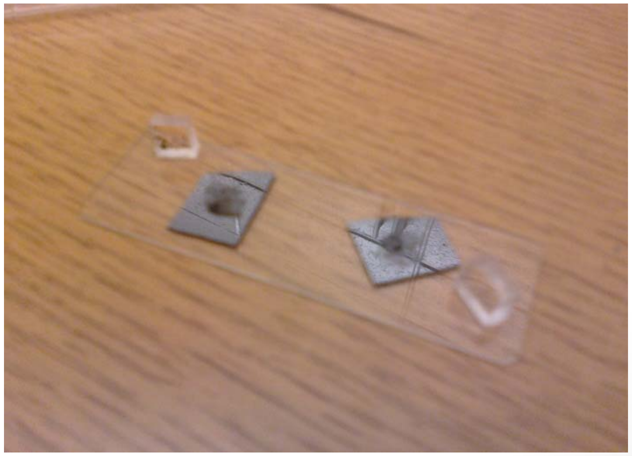
Spin coating- 1 layer

Drop cast- 1 drop

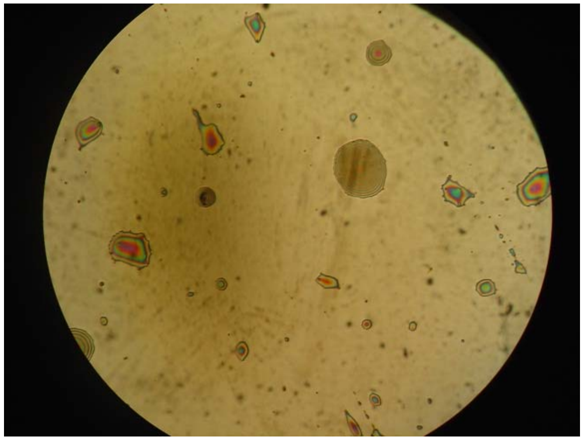


Microcontact Printing

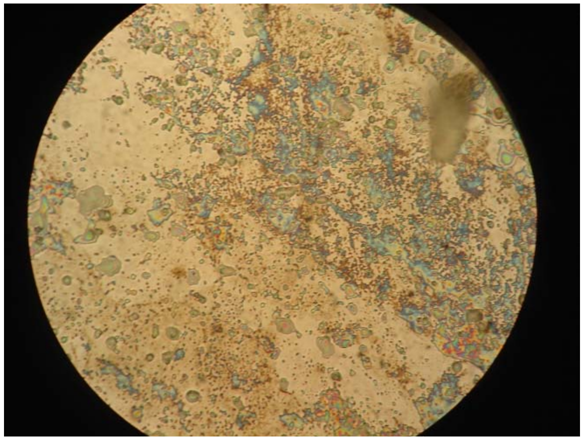
- Stamping nanoparticles onto substrate using polymer stamp
- Uneven distribution
- Optimum conditions?
- Needs a perfected technique
- Good with solutions with less organics (Pt, Au – hexane solutions)
- Good for larger particle size

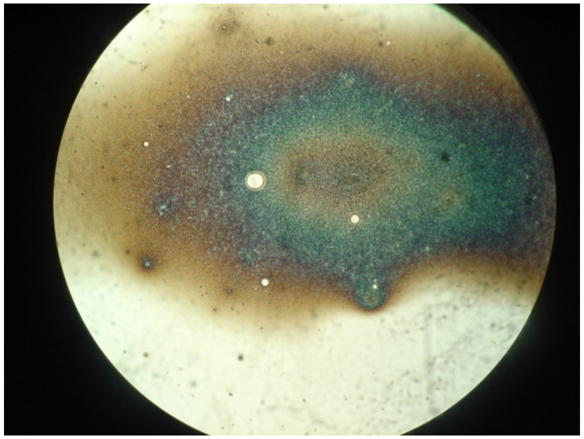
$Pt_{45}V_{18}Co_{37}$ Stamped, 3 drops vs drop-casting and after annealing



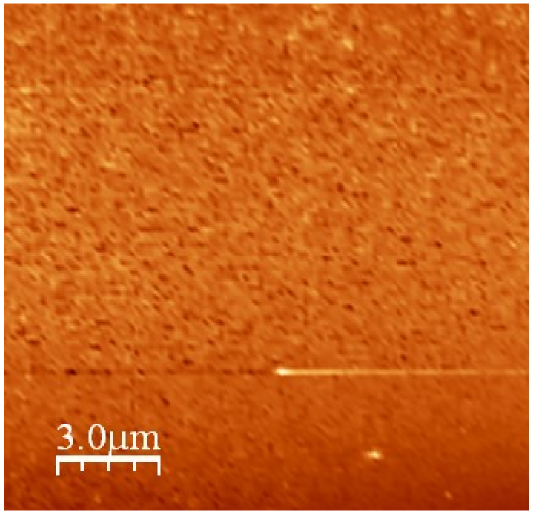
Drop cast, 3 drops, 100X magnification



Microcontact printing, 3 drops, 100X magnification



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

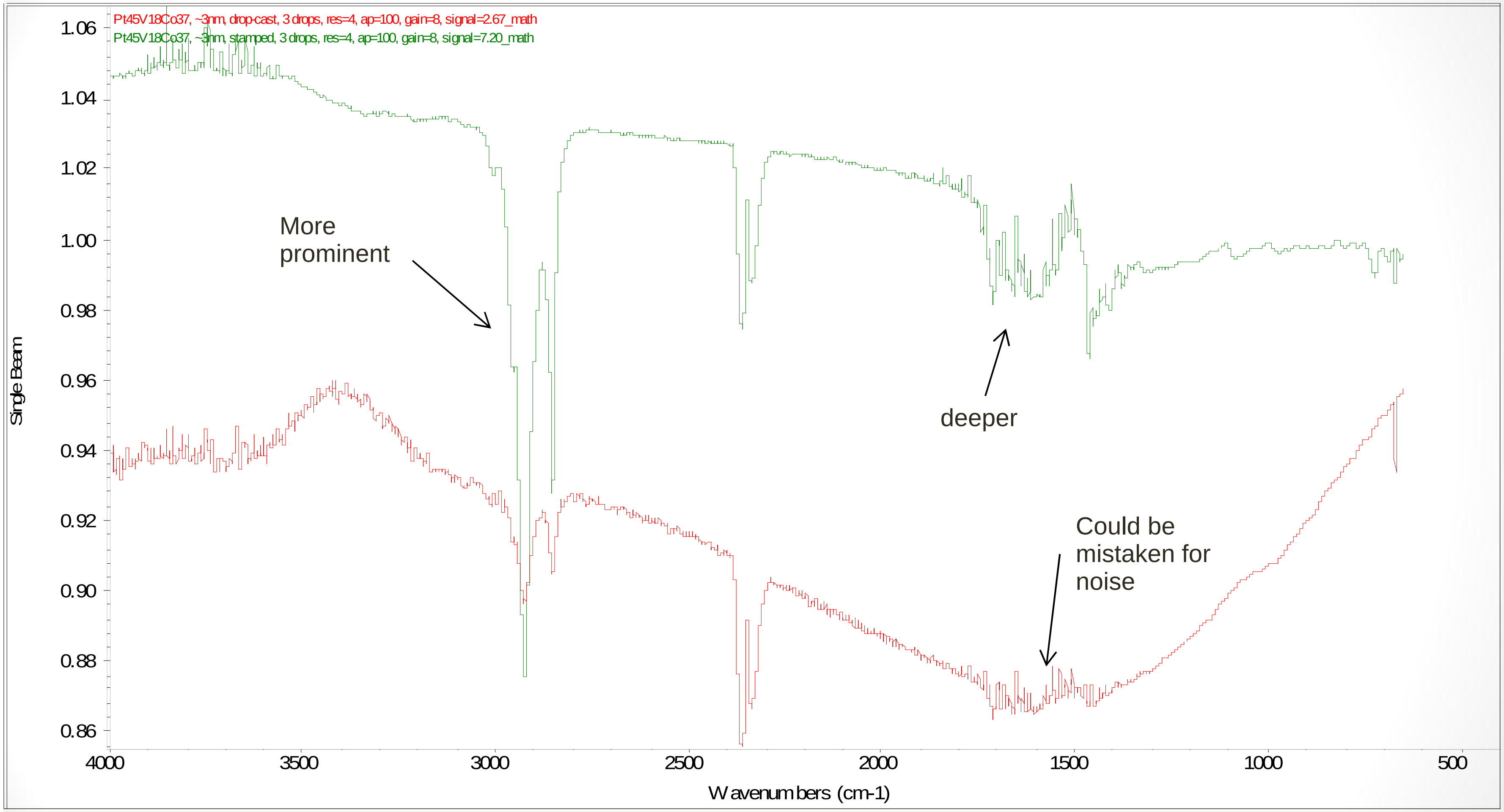


AFM of annealed sample
Thickness = ~200nm.

$Pt_{45}V_{18}Co_{37}$ Drop cast vs stamping

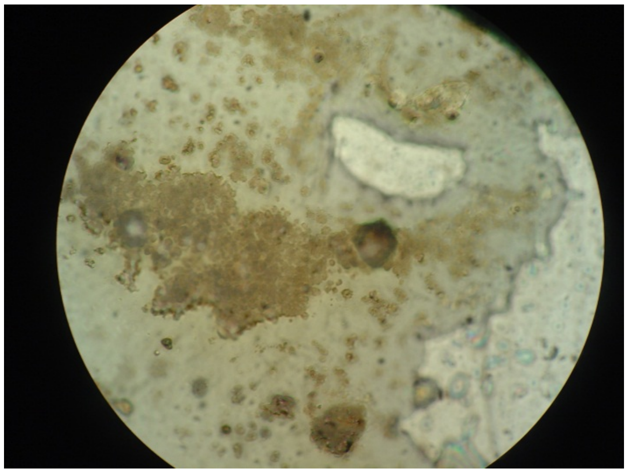
Stamped, 3 drops

Drop cast, 3 drops

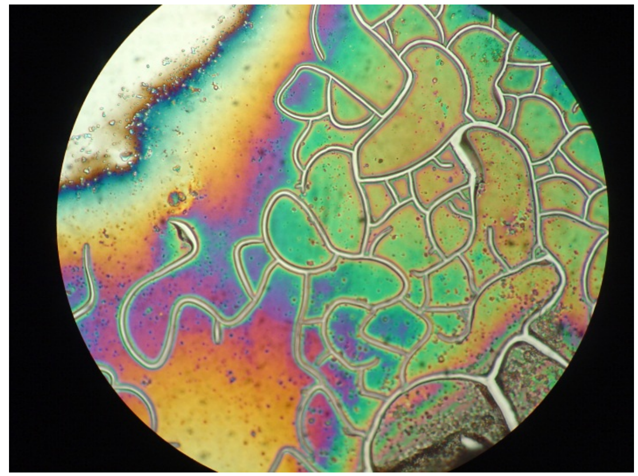


More particles on the stamped samples!

$Pt_{44}Ni_{14}Co_{42}$ 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?

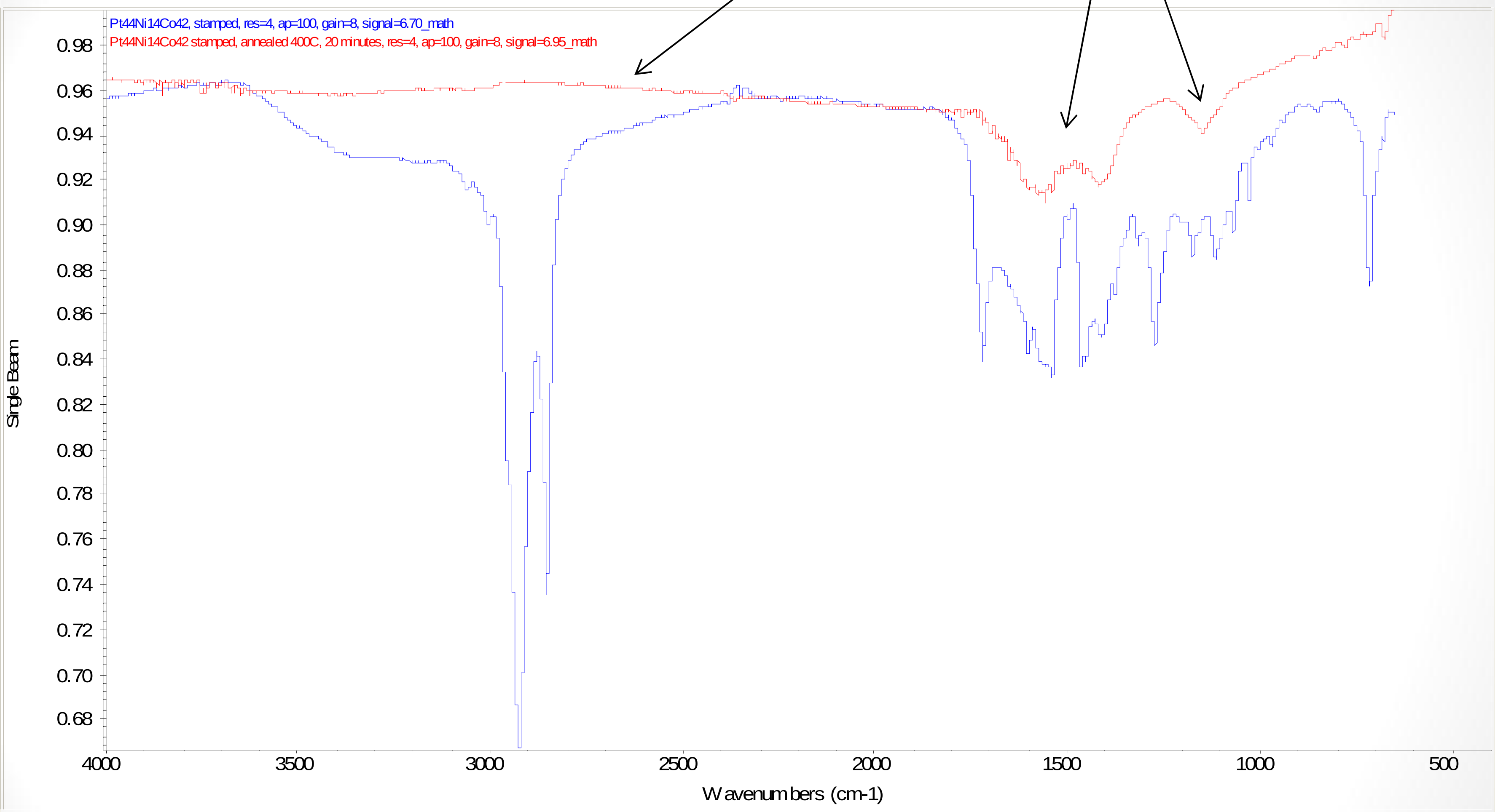
$Pt_{44}Ni_{14}Co_{42}$, stamped and annealed

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