Scale-Up of Carbon Nanotube Synthesis at the Jefferson Lab Free Electron Laser: From Research to Production

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ONR, State of Virginia, Luna Innovations

Why Make Carbon Nanotubes with the Jefferson Lab FEL?

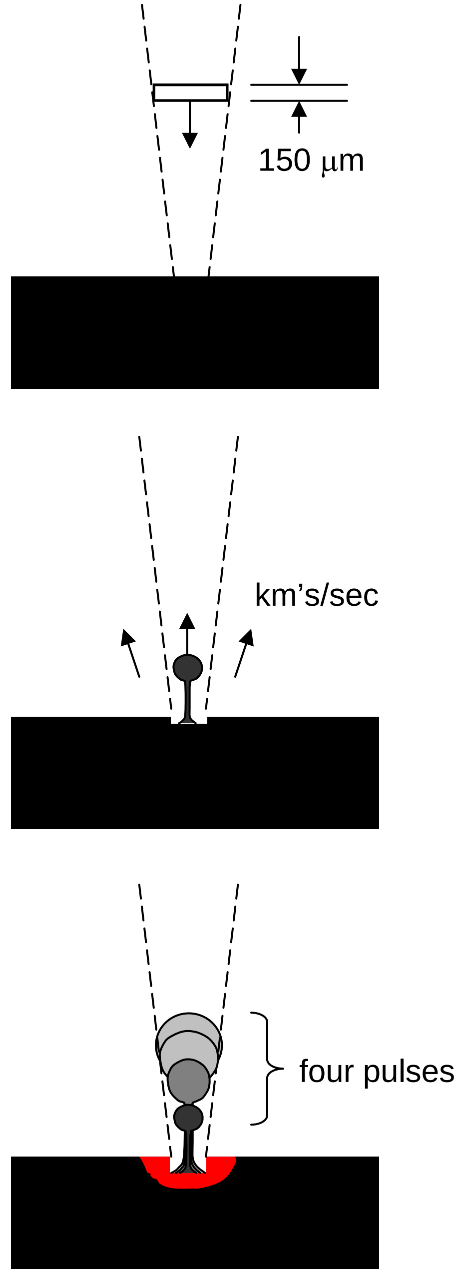
Laser Ablation/Oven technique makes the "best" material, but in tabletop form is limited to small quantities (<= 200 mg/hour with a typical pulsed Nd:YAG laser apparatus)…

Jlab FEL is unique, it has:

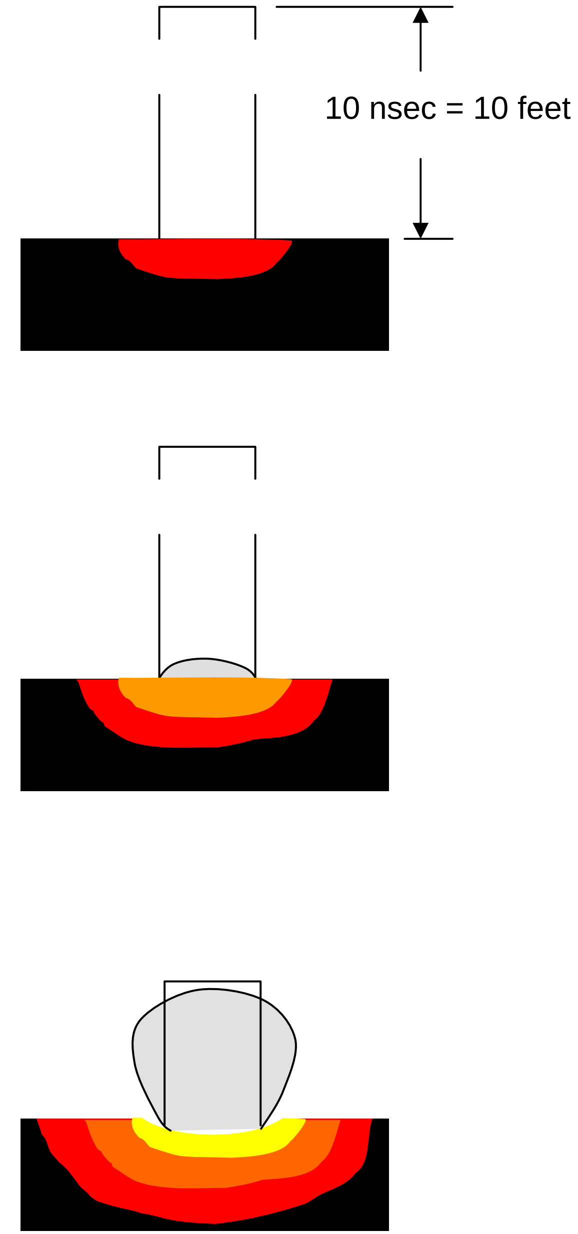
- ⇒ High average power (up to 10 kW)
- ⇒ Tunable wavelength
- ⇒ Underlying ultrafast pulse structure (sub-picosecond pulses at 9 MHz for the current work)

…can this give a high volume stream of nanoparticulate catalyst and highly excited carbon stock for nanotube formation?

FEL Ultrafast Ablation



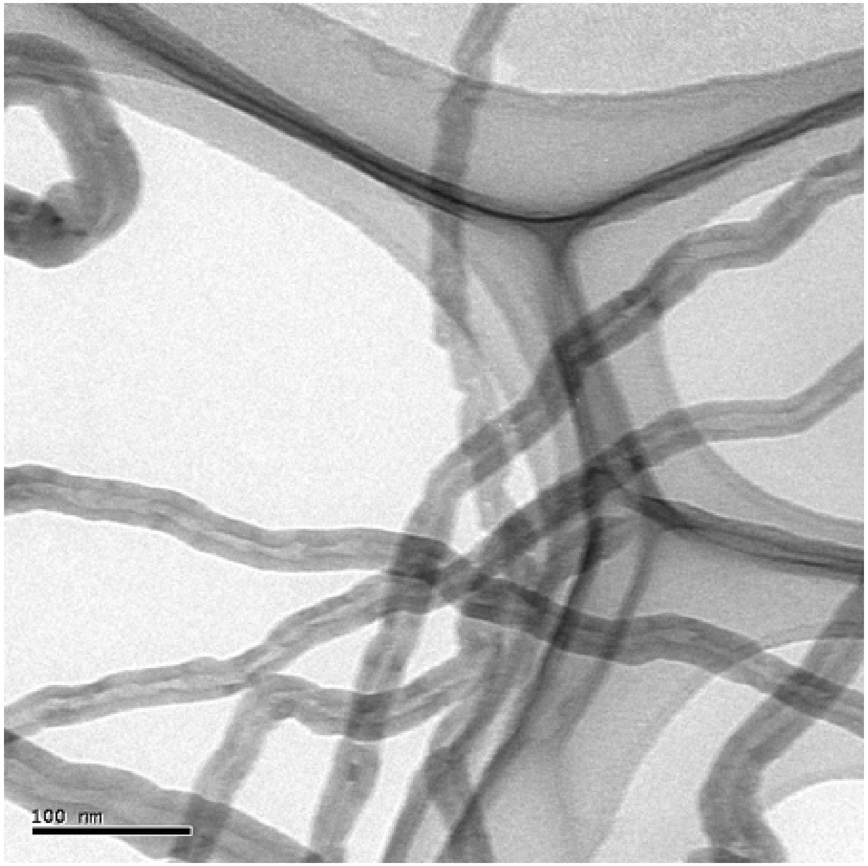
10-100 nsec Ablation



Desirable Nanotube Properties for Multi-functional Fiber-Reinforced Composites, (etc.)

- Single wall.
- Long.
- High Quality (clean, straight, defect-free walls).
- Pure/Purifiable.
- Dispersable.
- Specific Chirality (conduction and sensing).
- Specific Diameter (bonding and intermolecular interactions)

Low "Quality" Nanotubes (bulk Chinese product)



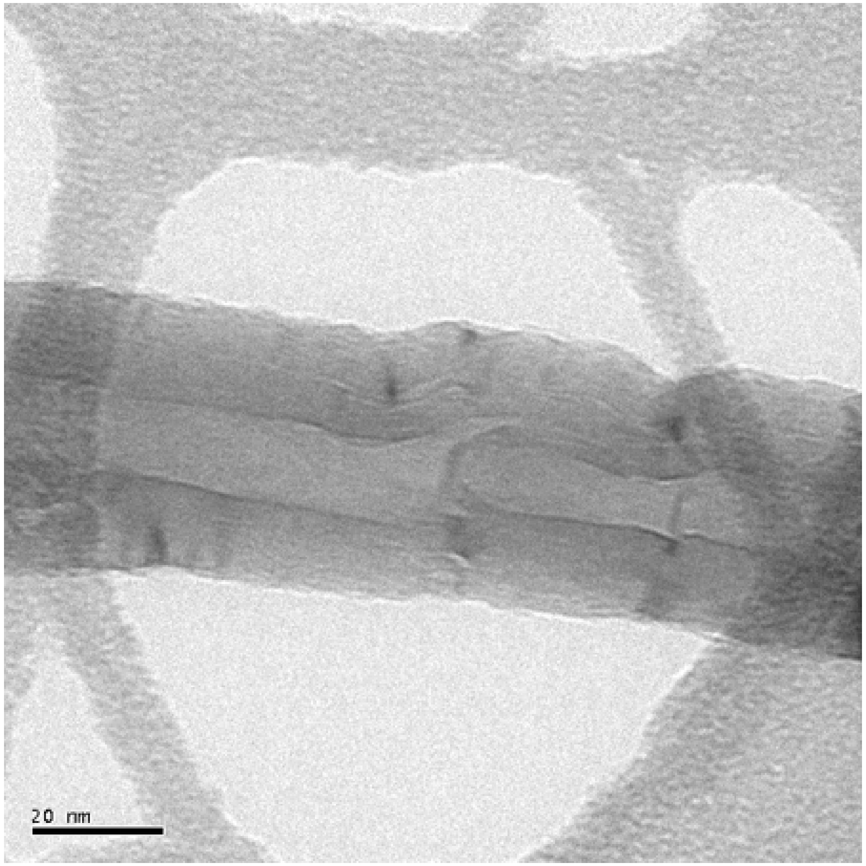


Image Credits: Dr. Roy Crooks (Swales/NASA LaRC),
Contributed via Cheol Park (NIA/NASA LaRC)

High Res SEM, 2005 FEL Raw Material

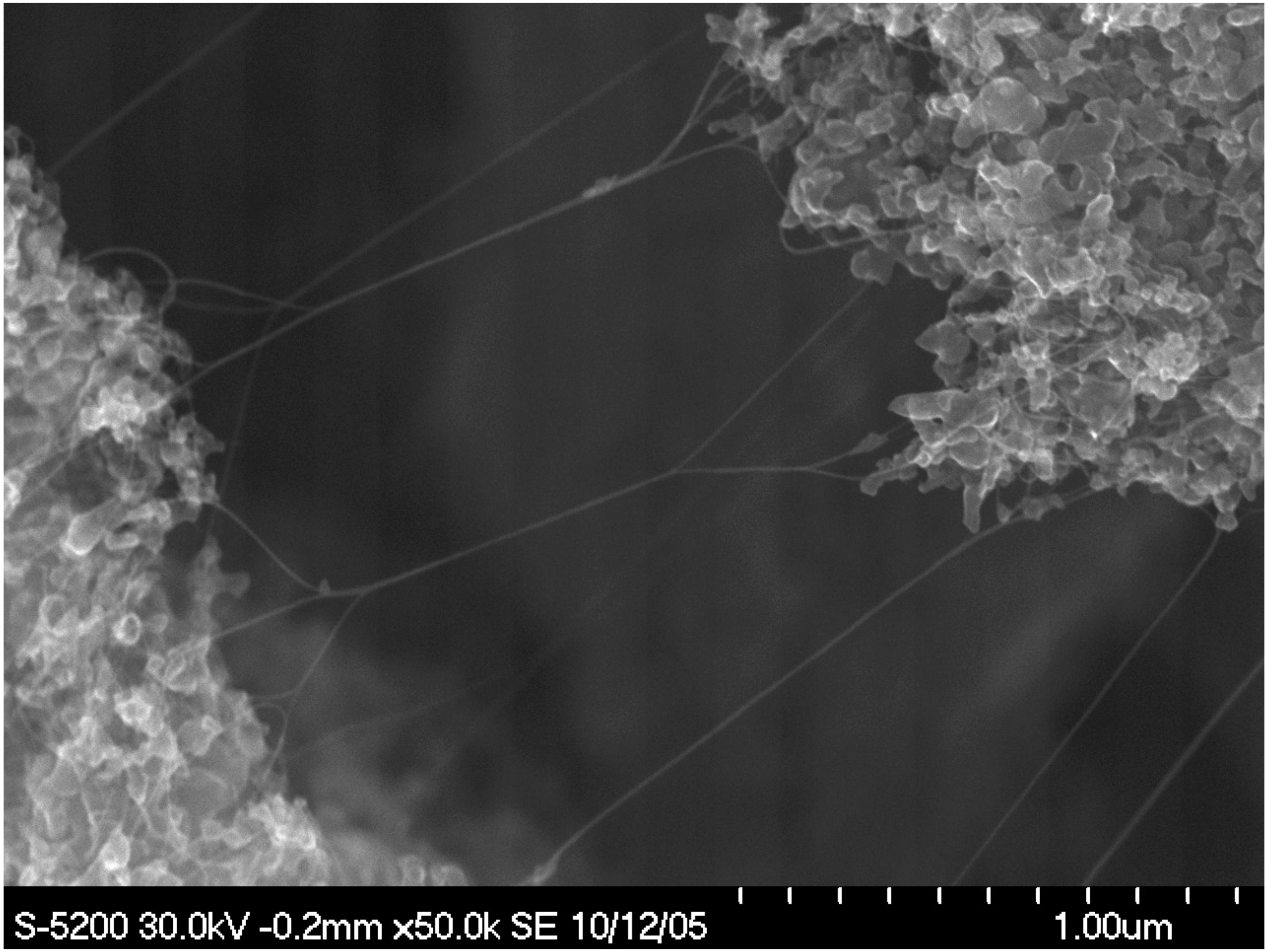


Image Courtesy: Ron Quinlan, College of William and Mary

High Res SEM, 2005 FEL Raw Material

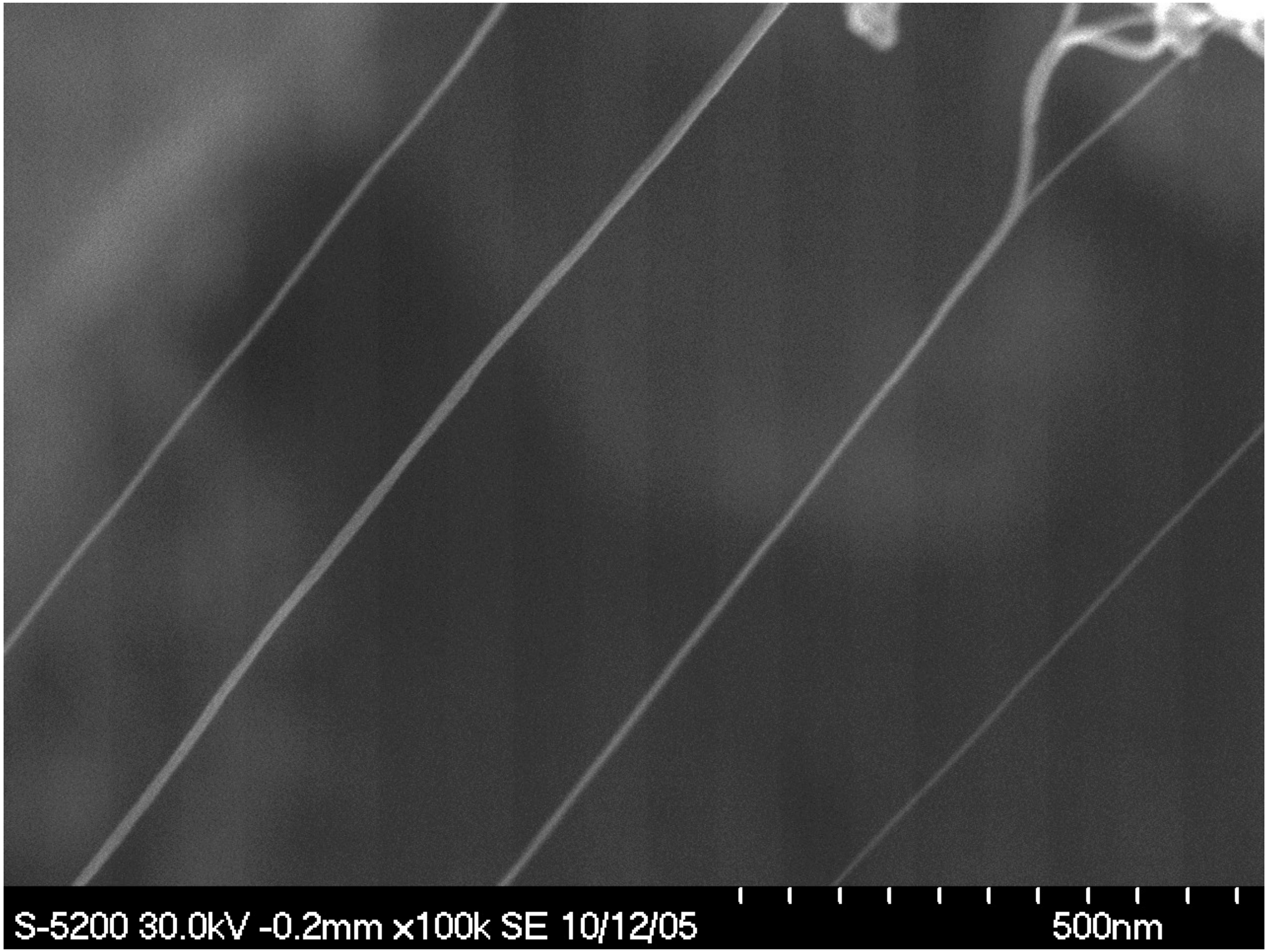
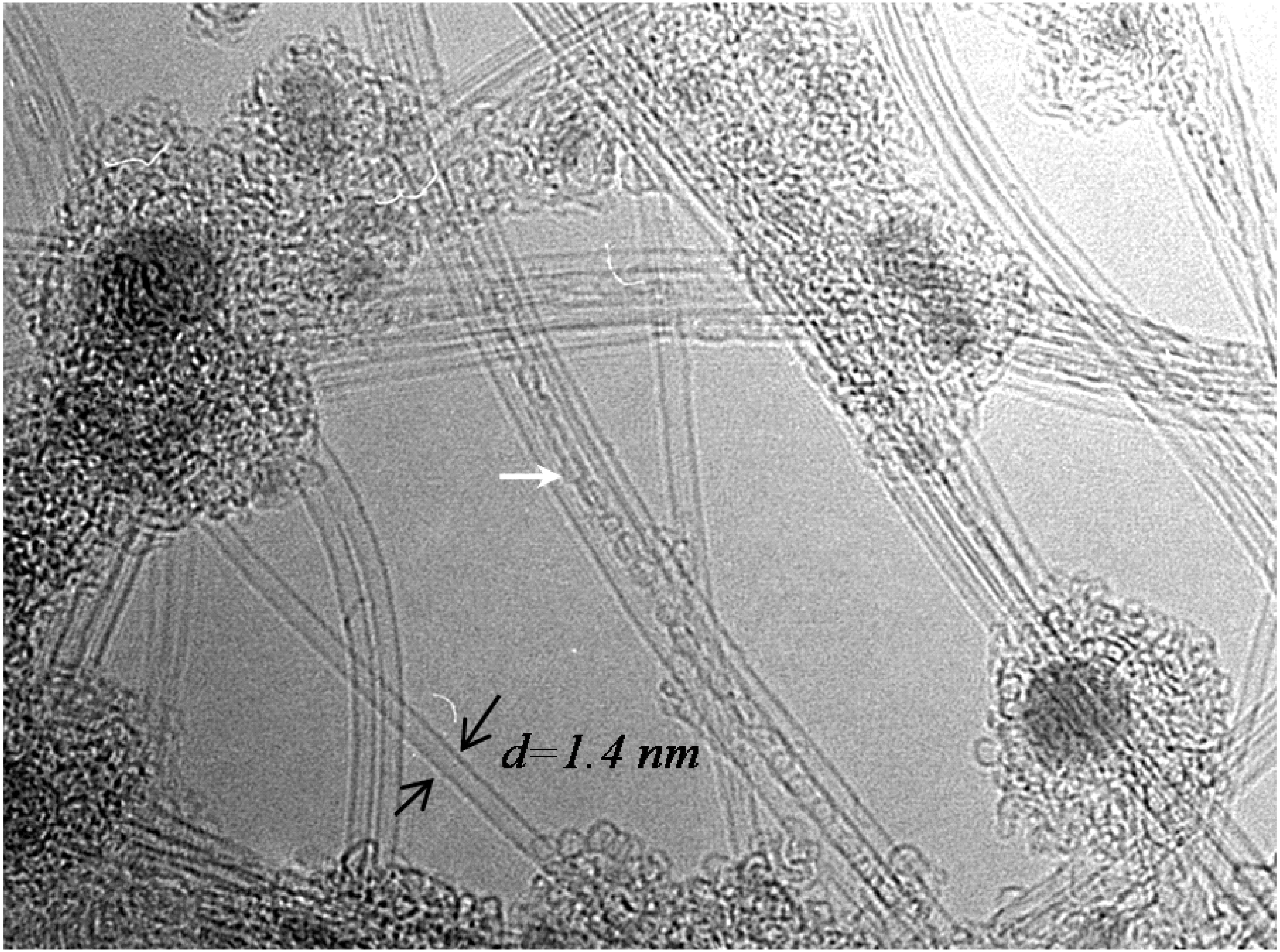
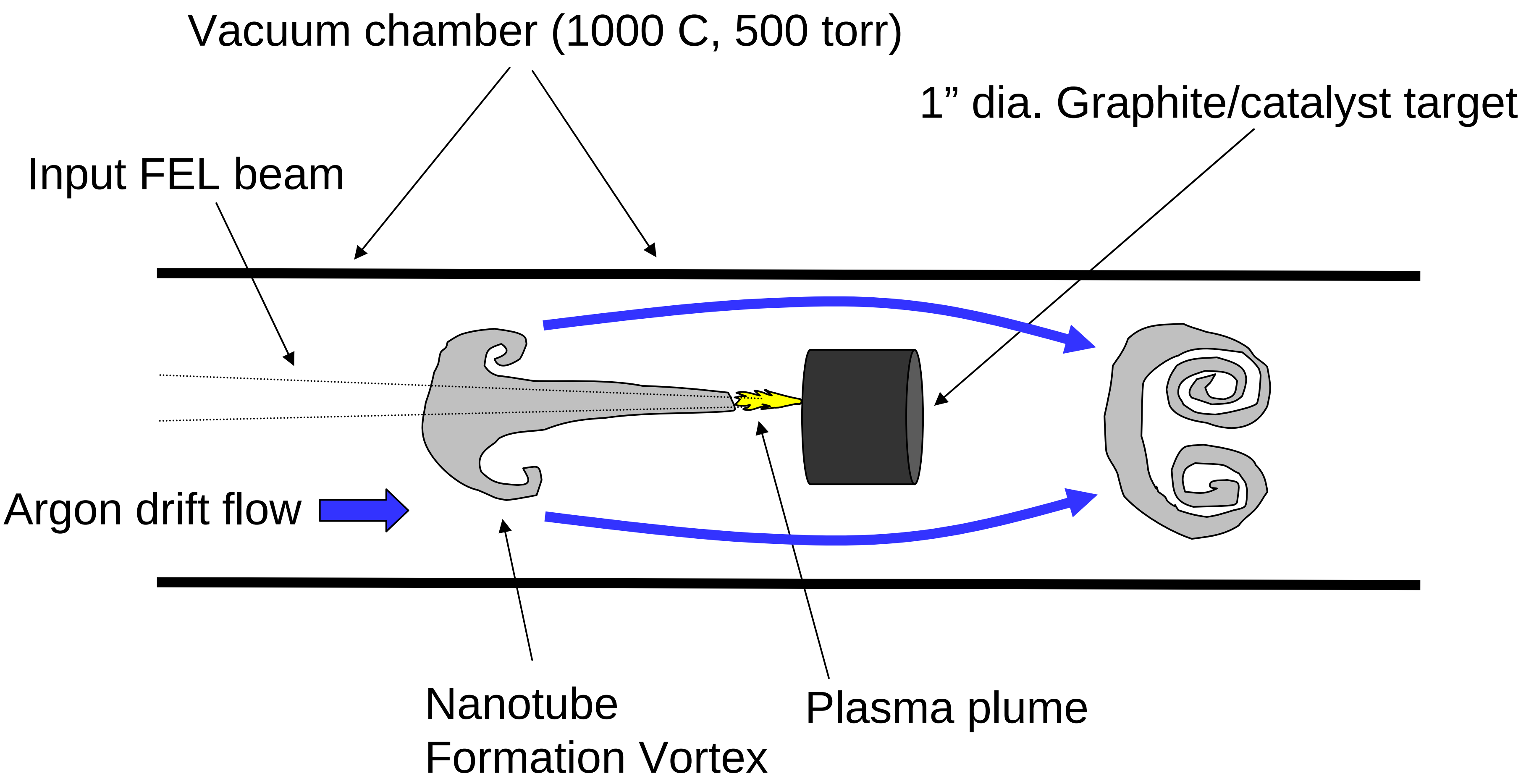


Image Courtesy: Ron Quinlan, College of William and Mary

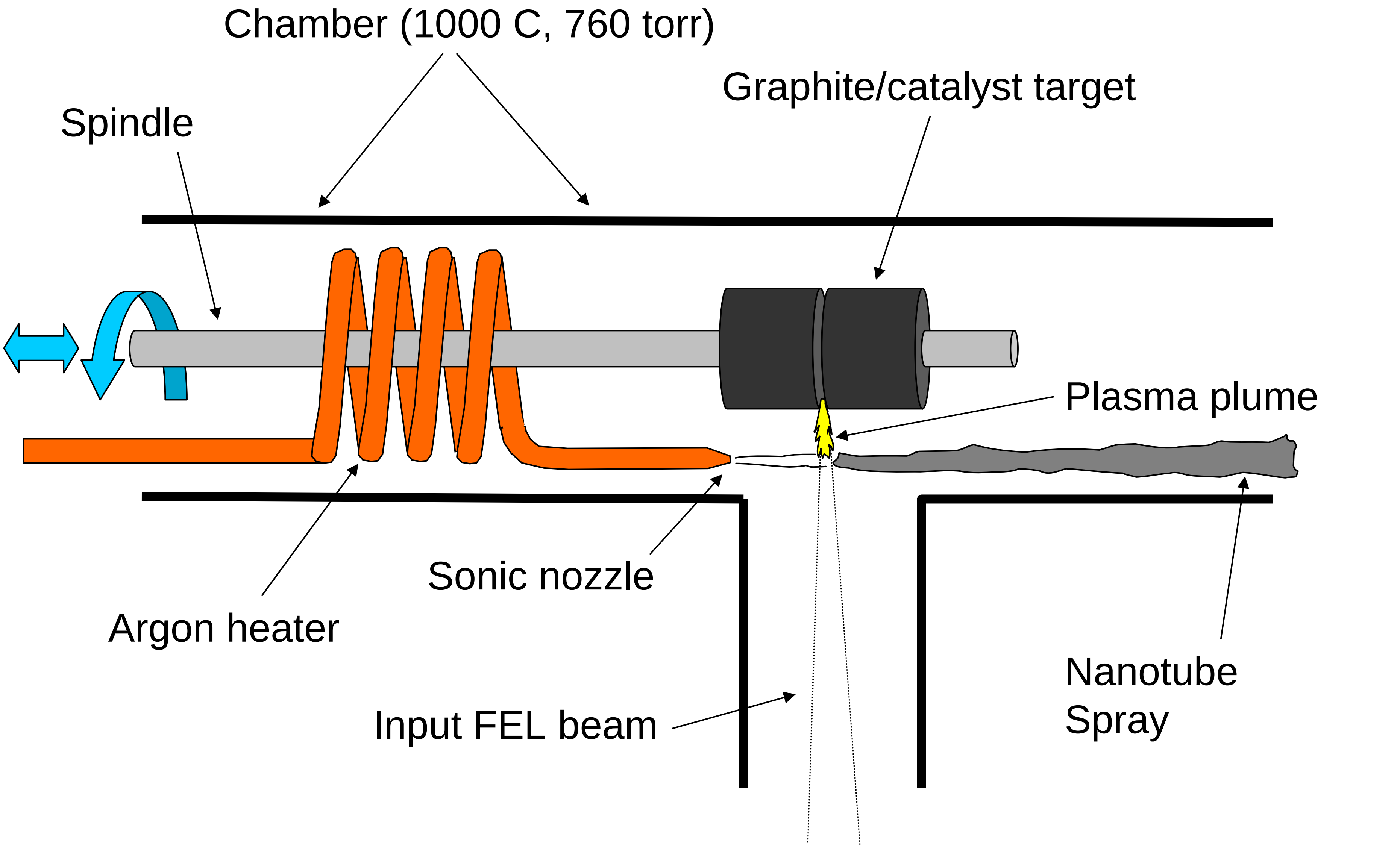
High Resolution TEM (2001) FEL Material Shows Single Walls of Individual Tubes



Original Front-Pumped Chamber (2000-2001)

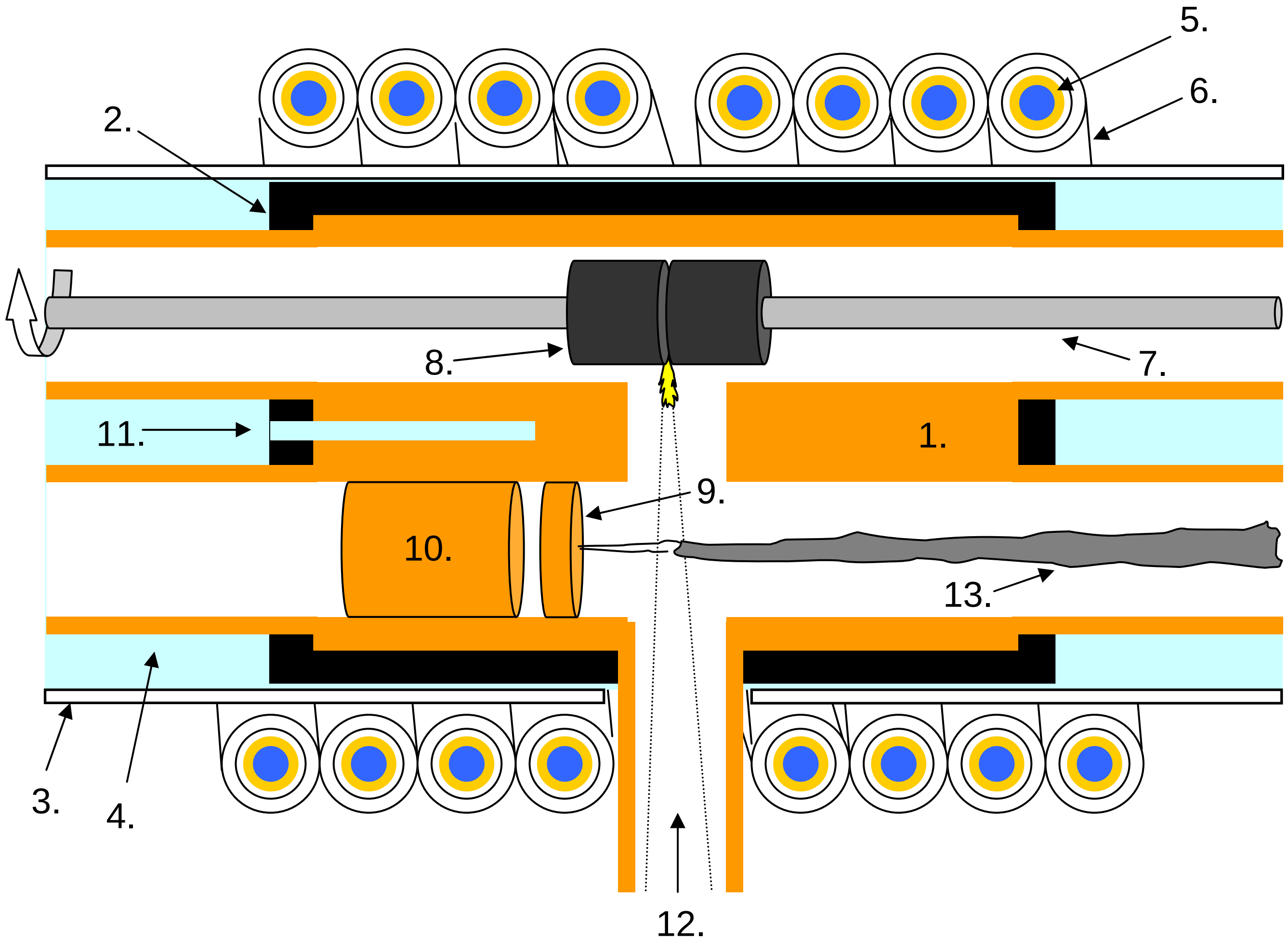


Schematic of First Side-Pumped Synthesis Chamber (2001, shutdown)

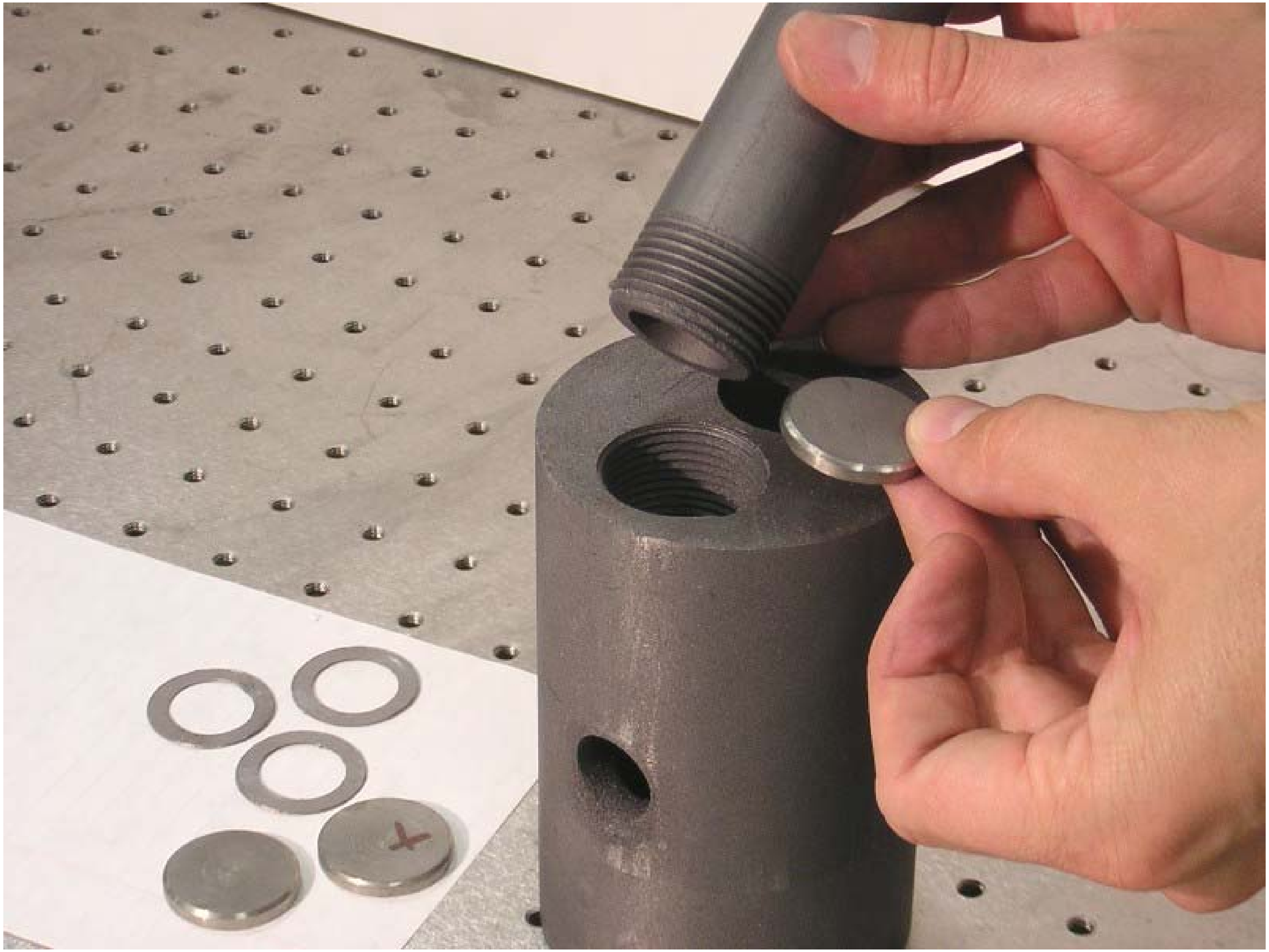


Schematic RF-Induction Heated Side-Pumped Synthesis Chamber (2005-present)

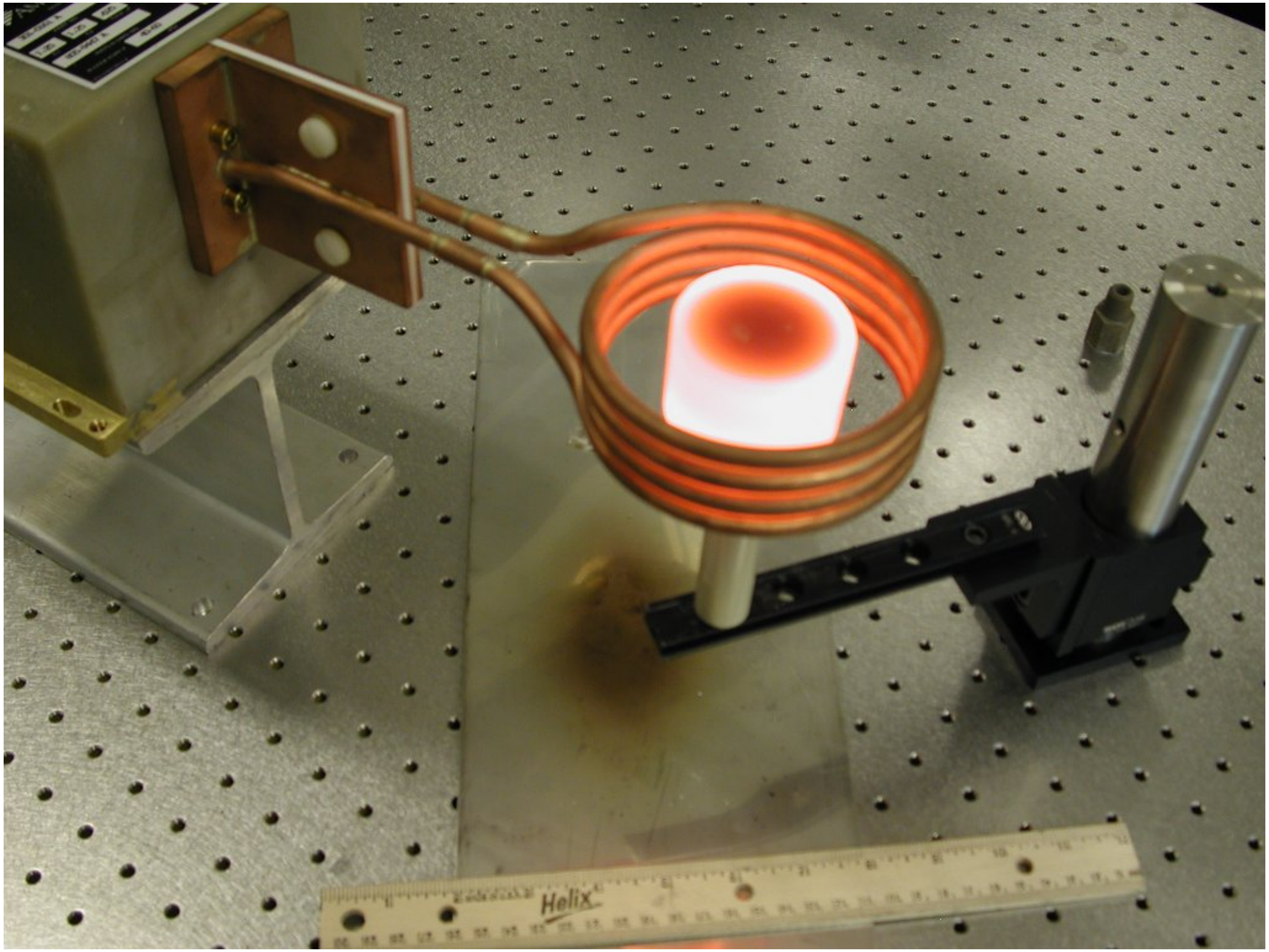
1. Graphite core
2. Insulation
3. Purge vessel
4. Purge gas
5. 3.5 kW RF coil
6. Insulation
7. Spindle
8. Target w/catalyst
9. Orifice plate
10. Porous plug heater
11. Pyrometer port
12. Input FEL beam
13. Nanotube spray



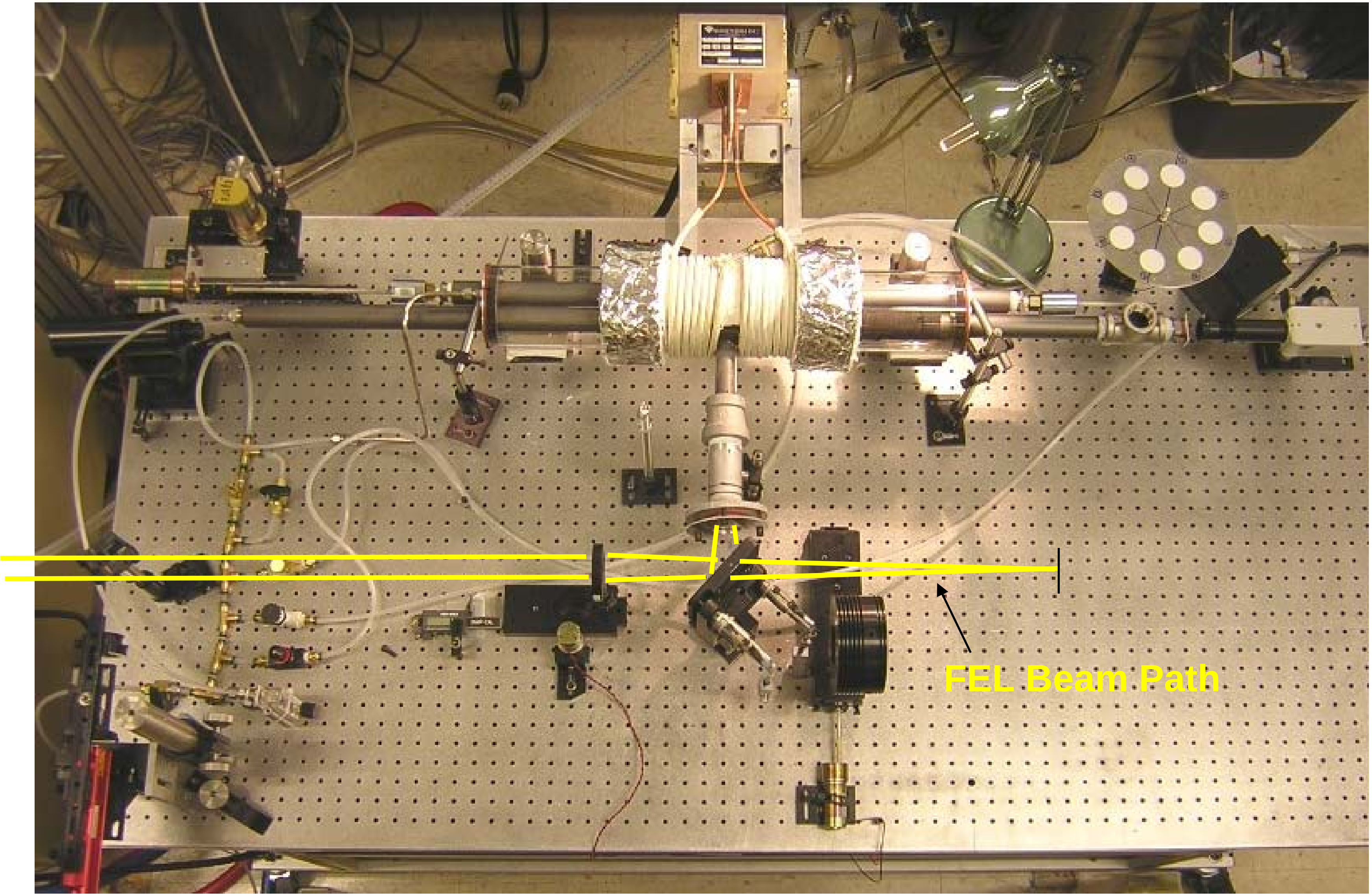
Chamber Core with Orifice Plate



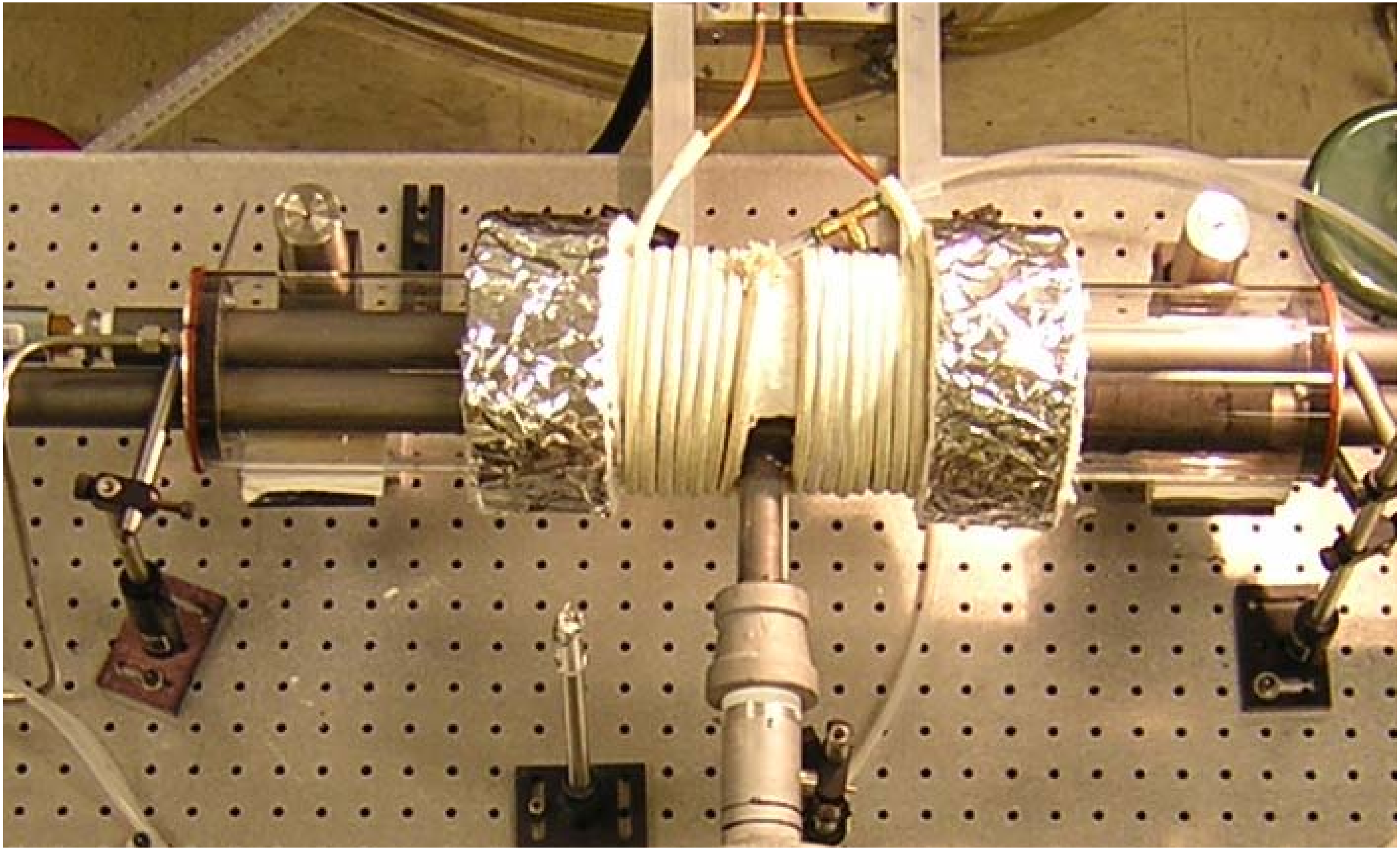
7.5 kW Induction Heater with Graphite Test Block



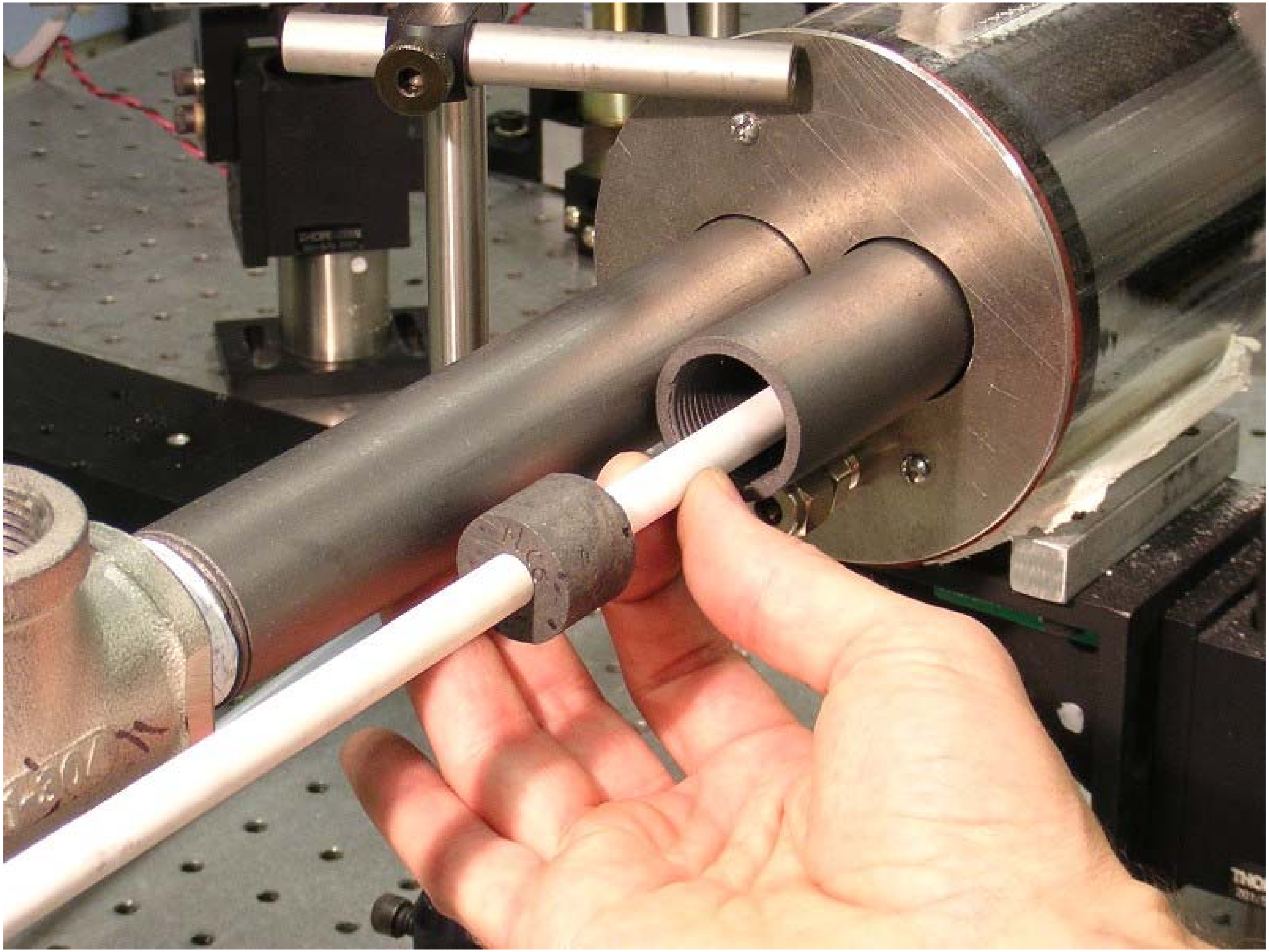
Apparatus, Overhead View



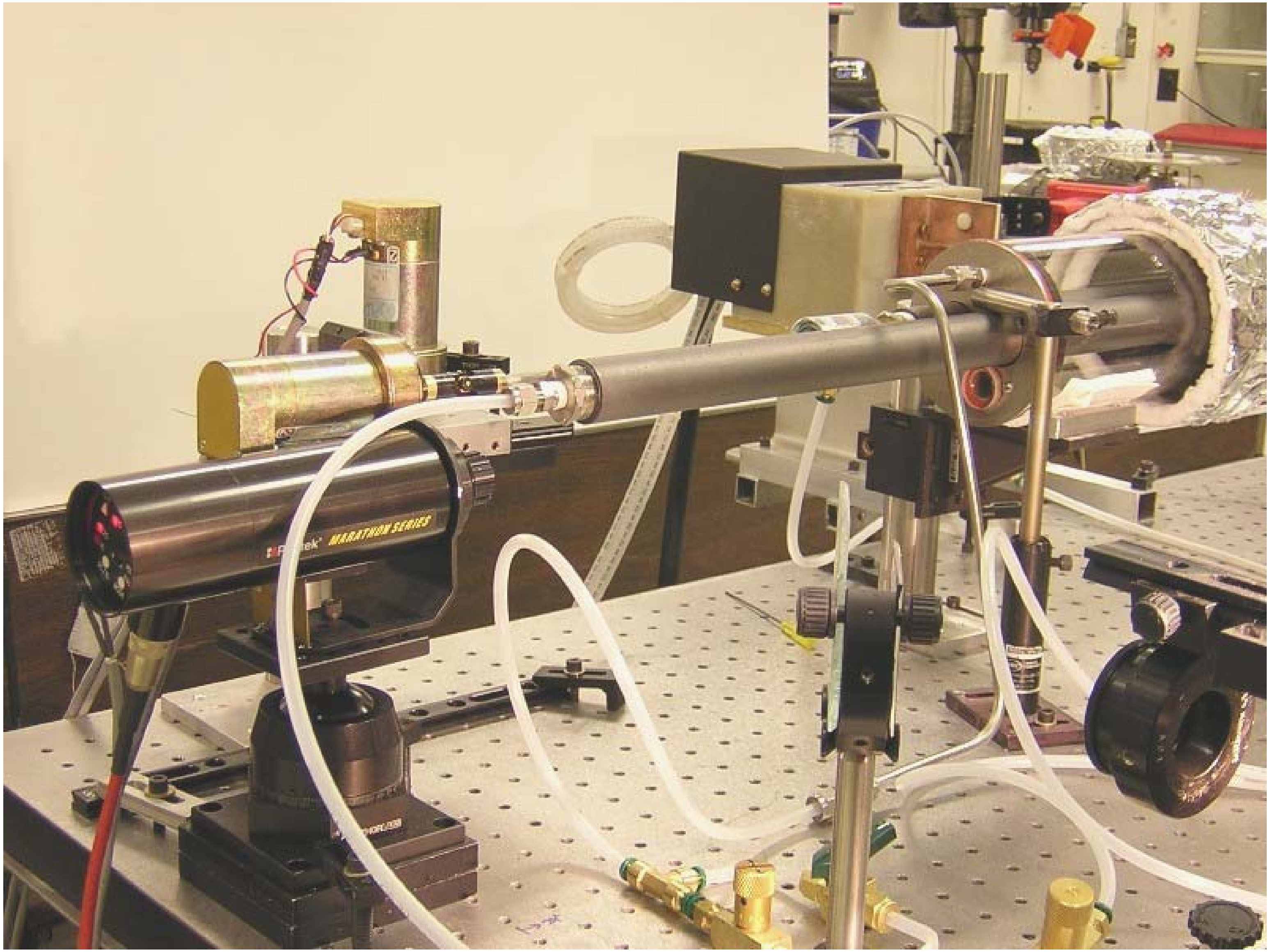
Chamber, Hot Zone



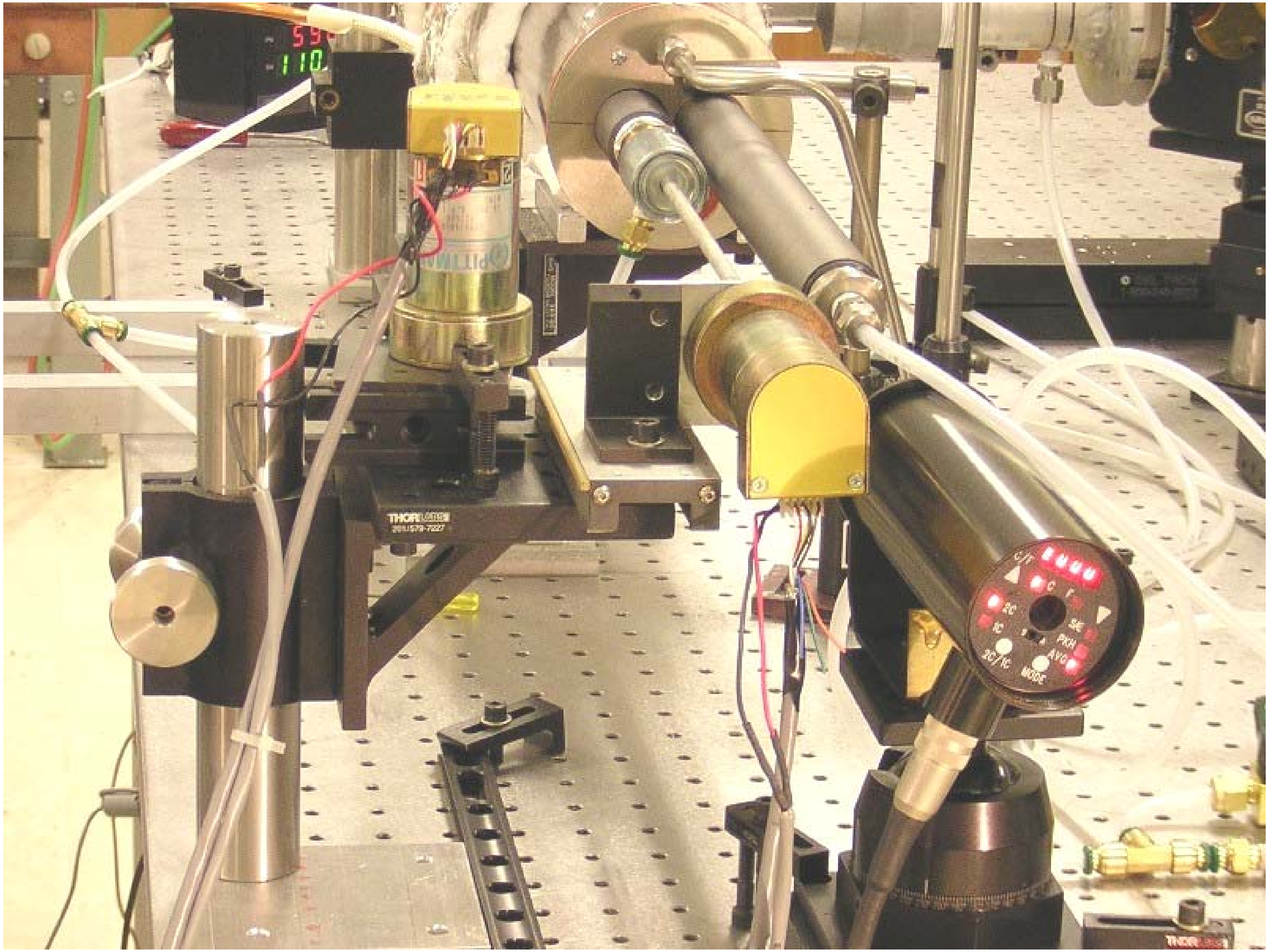
Target Loading



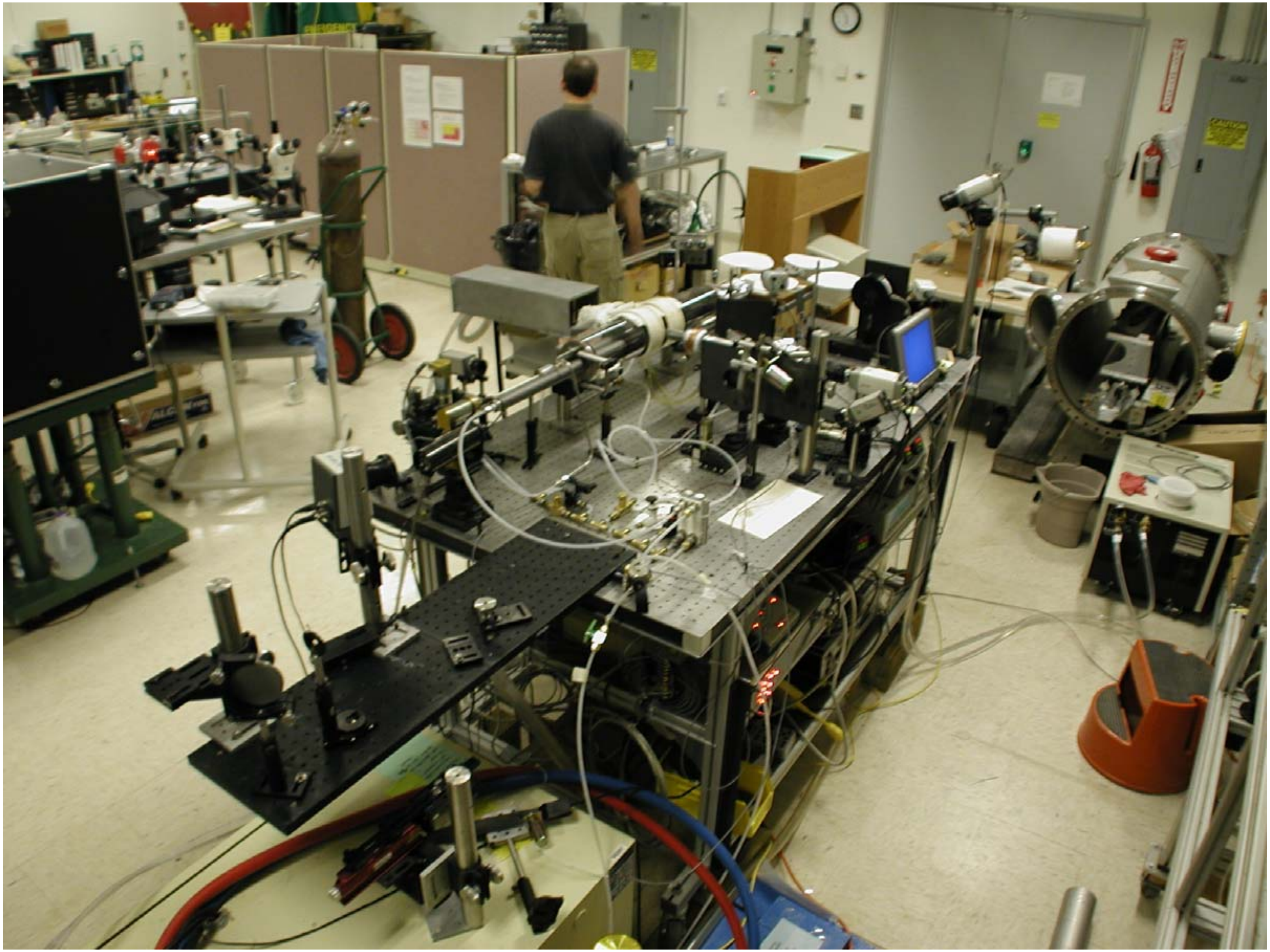
Chamber, Upstream End



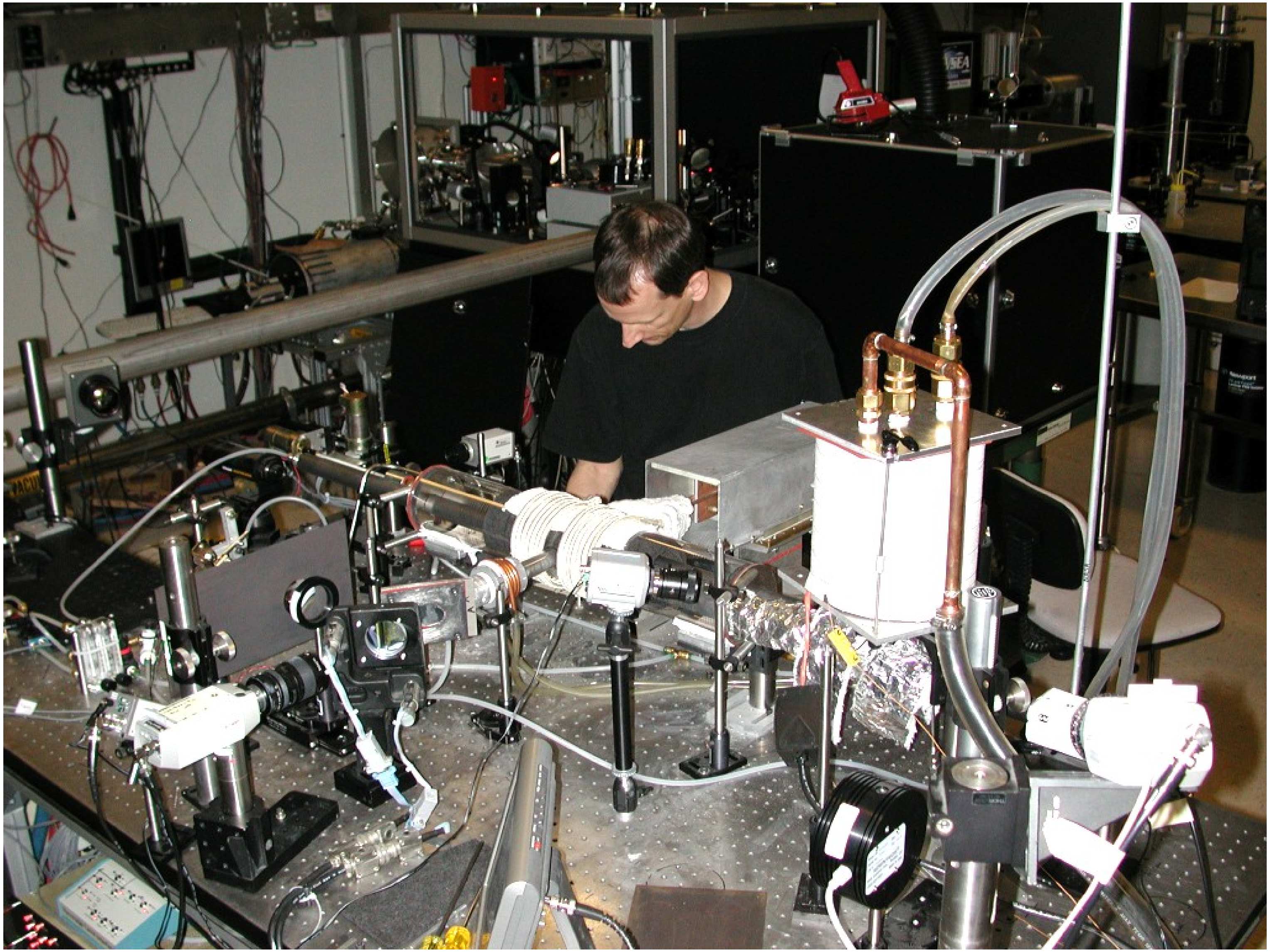
Chamber, Upstream End



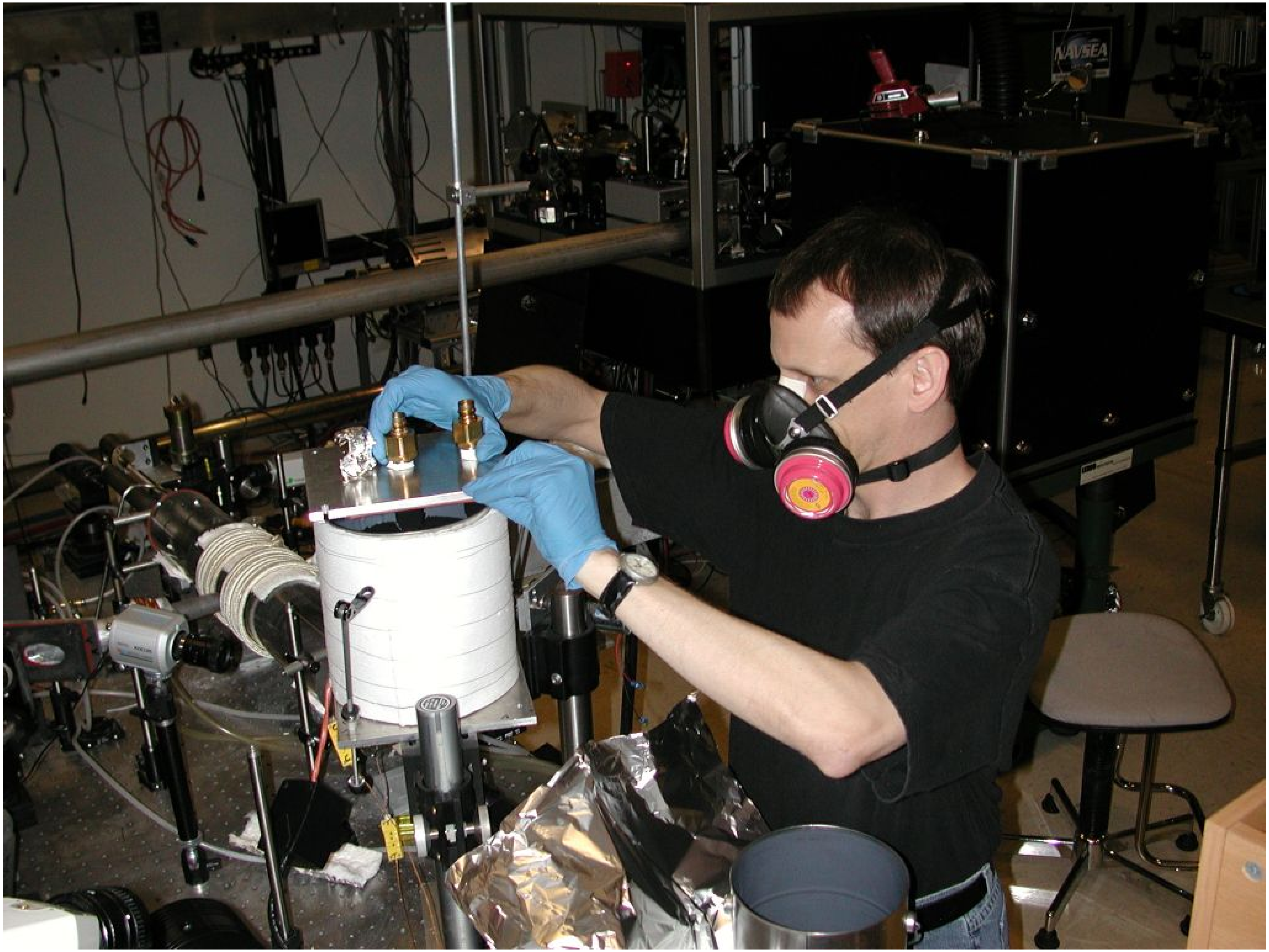
8/05, Rig installed in Lab 1



8/05, Rig installed in Lab 1



8/05, Opening Production Collector

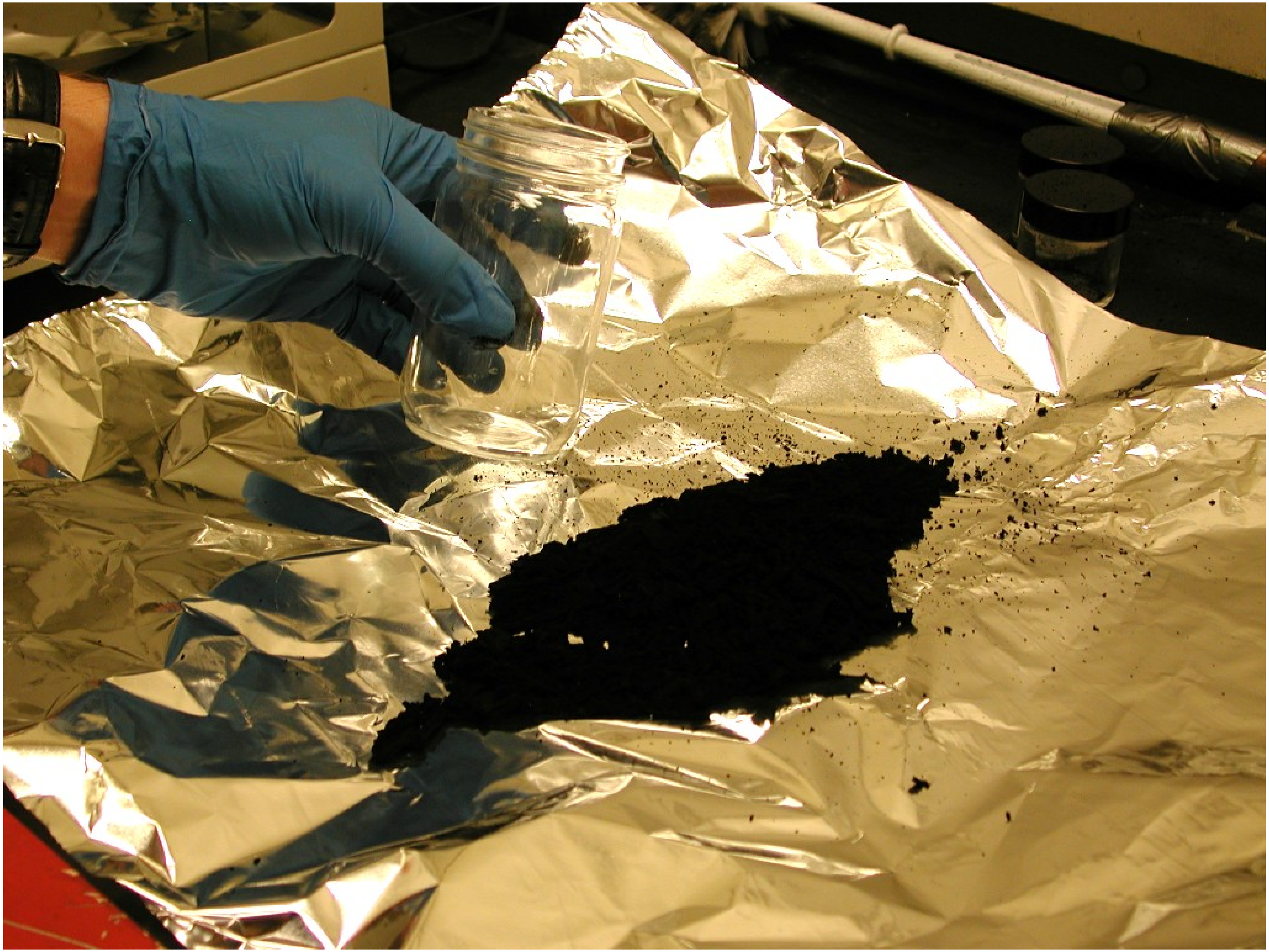


8/05, Collector with 1 gram raw SWNT

8/05, Laden Collector

8/05, Cleaning Collector

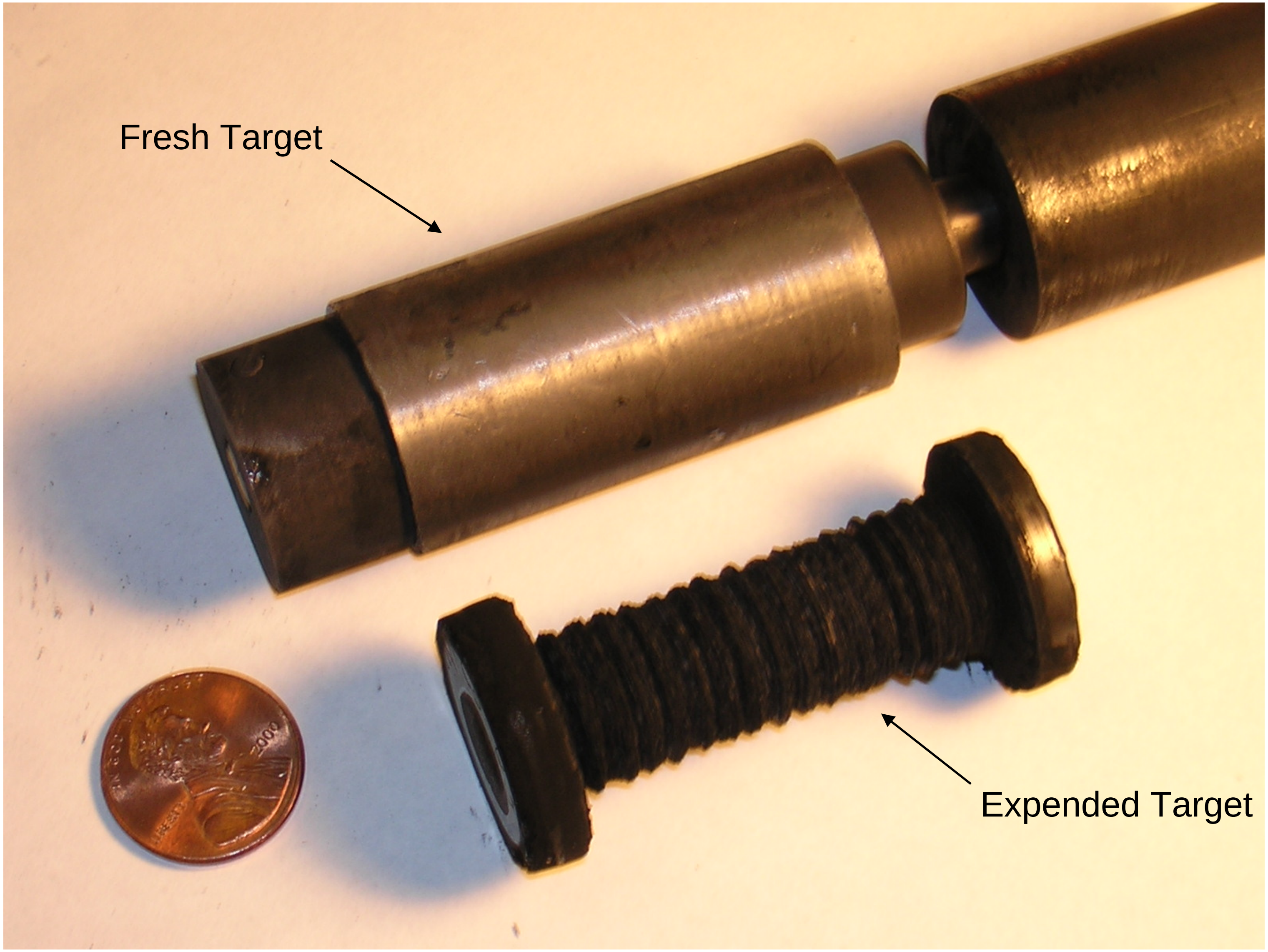
8/05, Couple of grams of raw SWNT



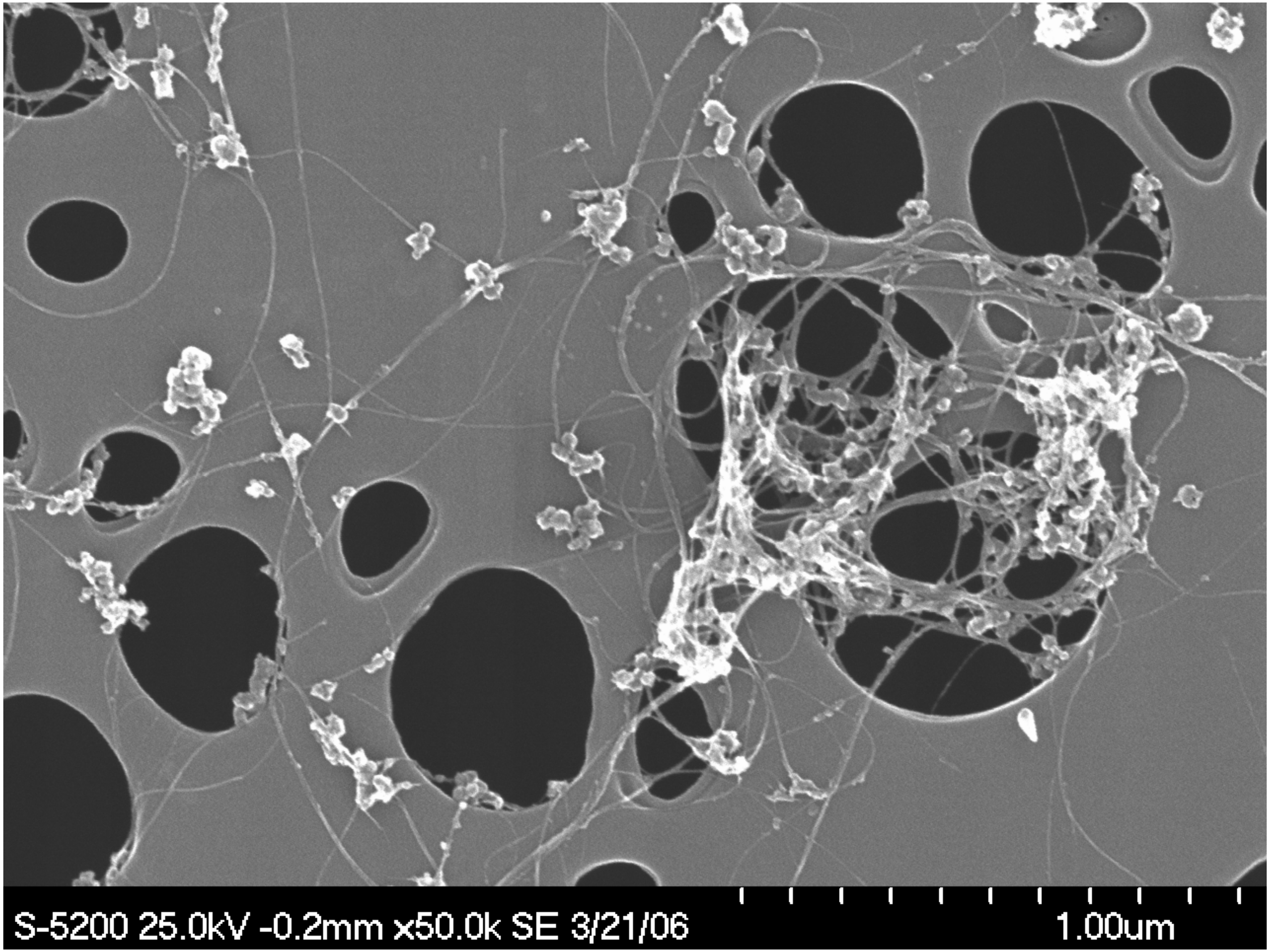
8/05, Raw SWNTs in the jar,
One Hour Exposure, Yield ~10%

4/05/06, 7.5 grams Raw Material Collected 1.25 Hour Exposure, Est. Yield 50-80%

4/05/06, Used Target, 75 Minutes Elapsed Time



SEM of Current High Yield Raw Material on Holey Carbon Substrate



…A Brief Digression on the Application of Raman Spectroscopy to the Analysis of Single Walled Carbon Nanotubes…

High Res SEM, June 2005 Raw Material

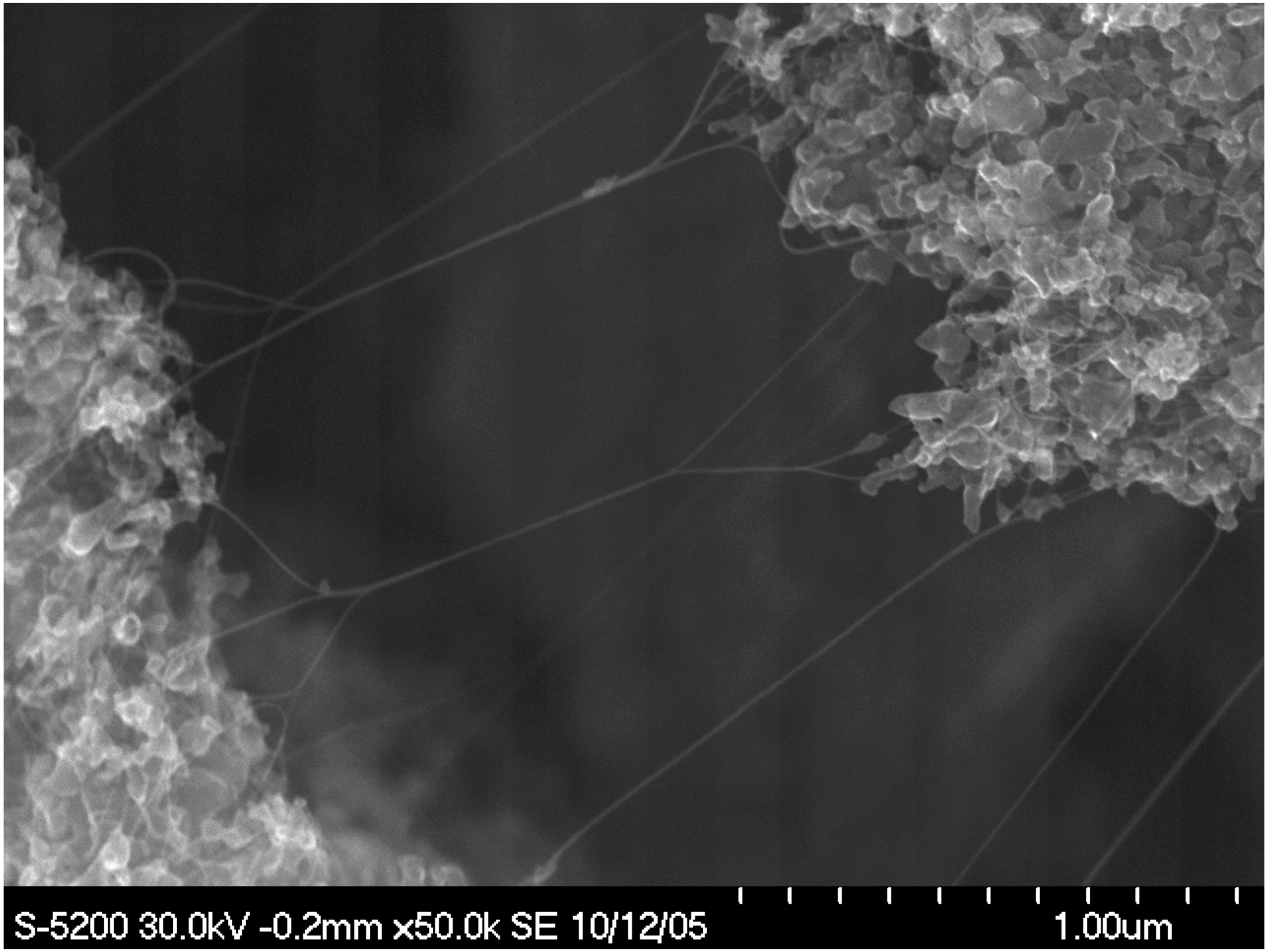
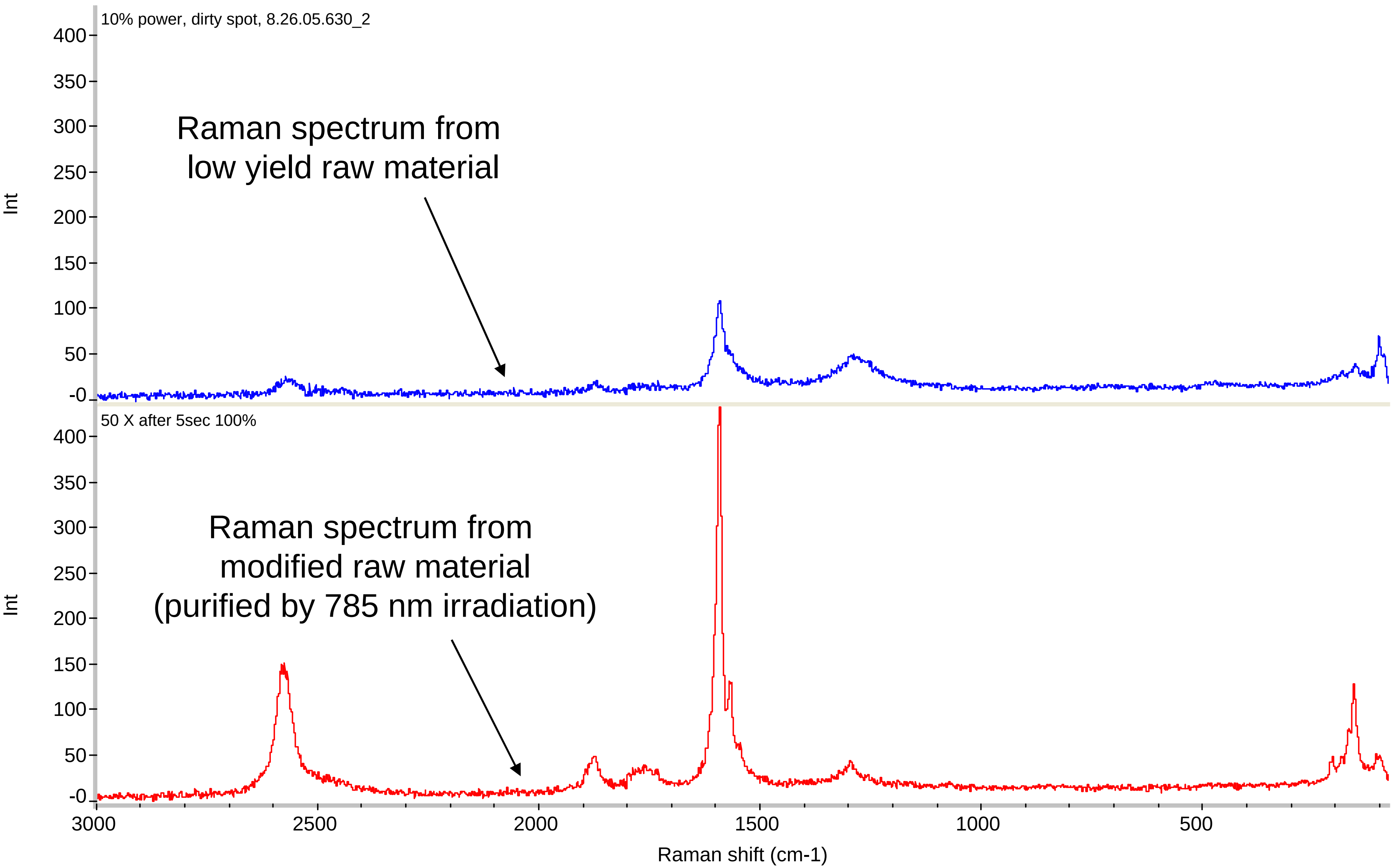


Image Courtesy: Ron Quinlan, College of William and Mary

Laser Purification of August 2005 SWNT, 785 nm



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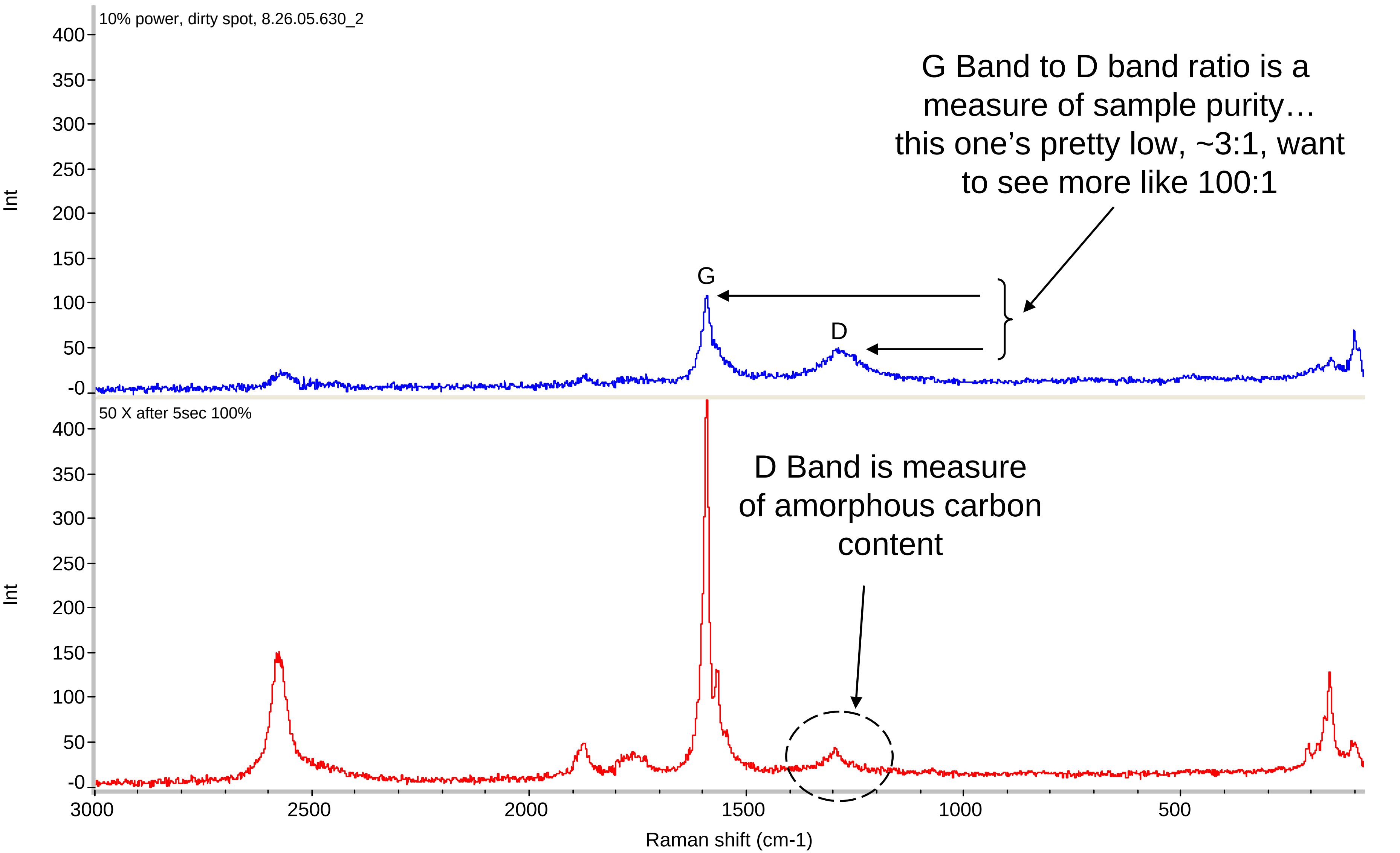

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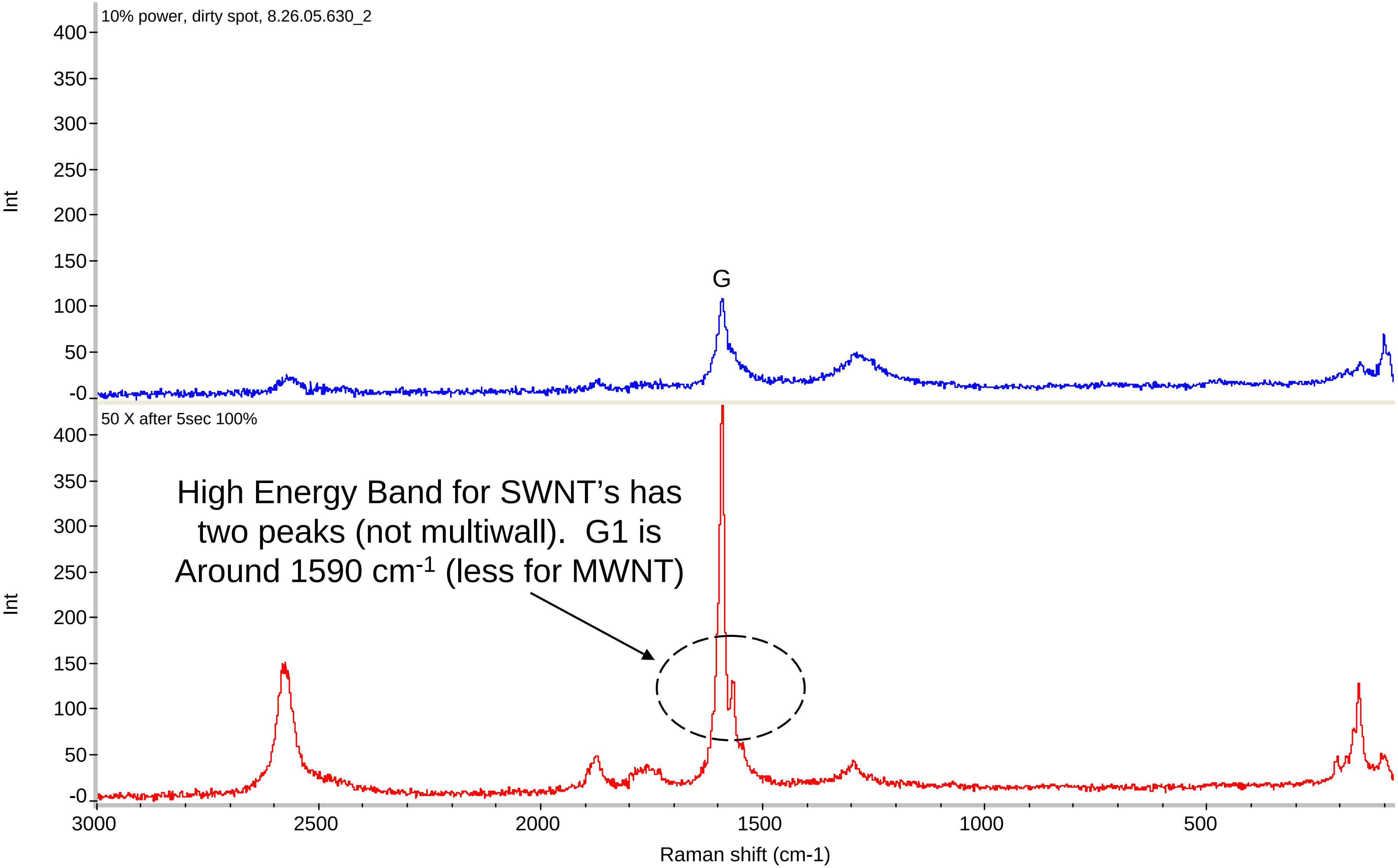

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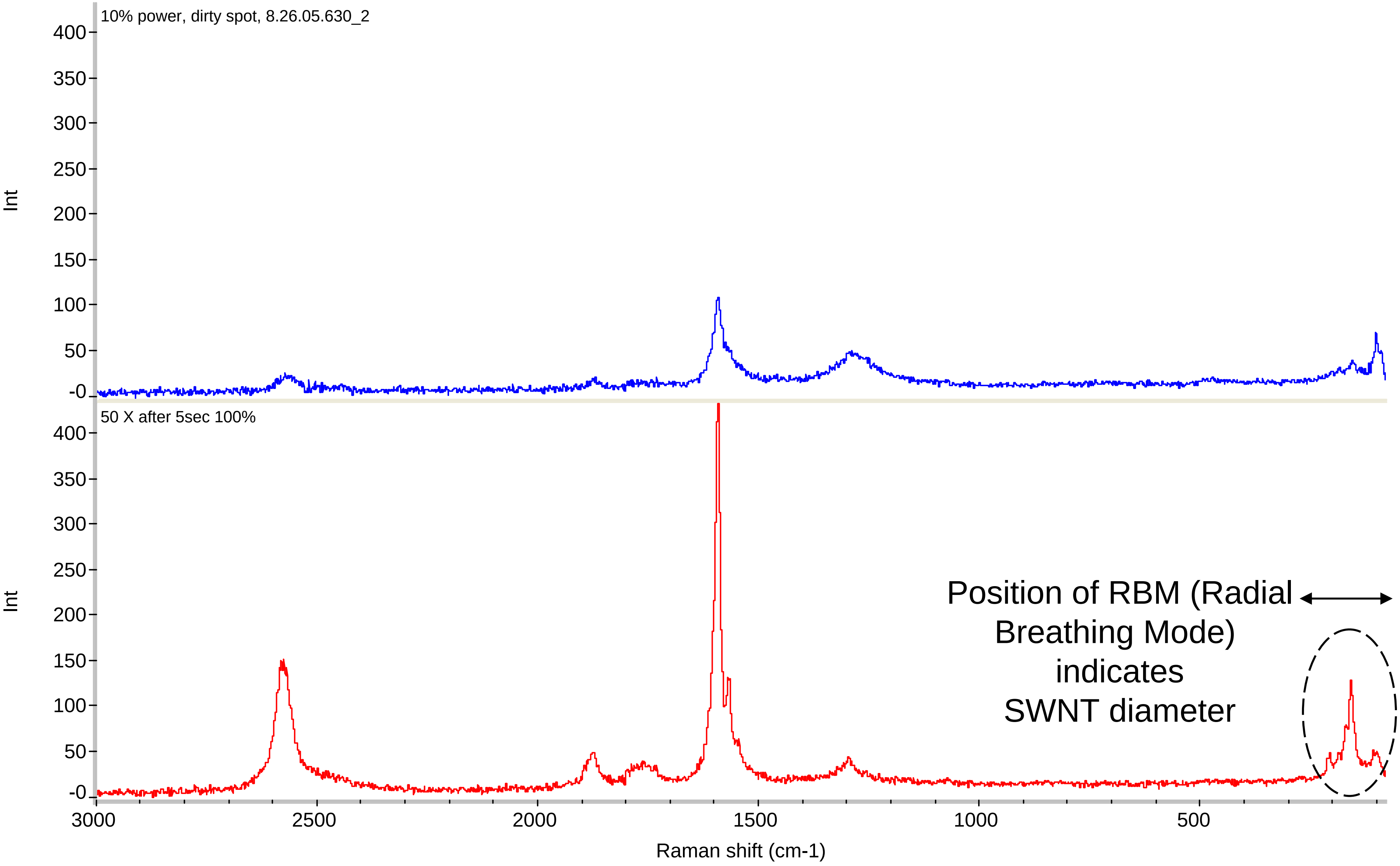

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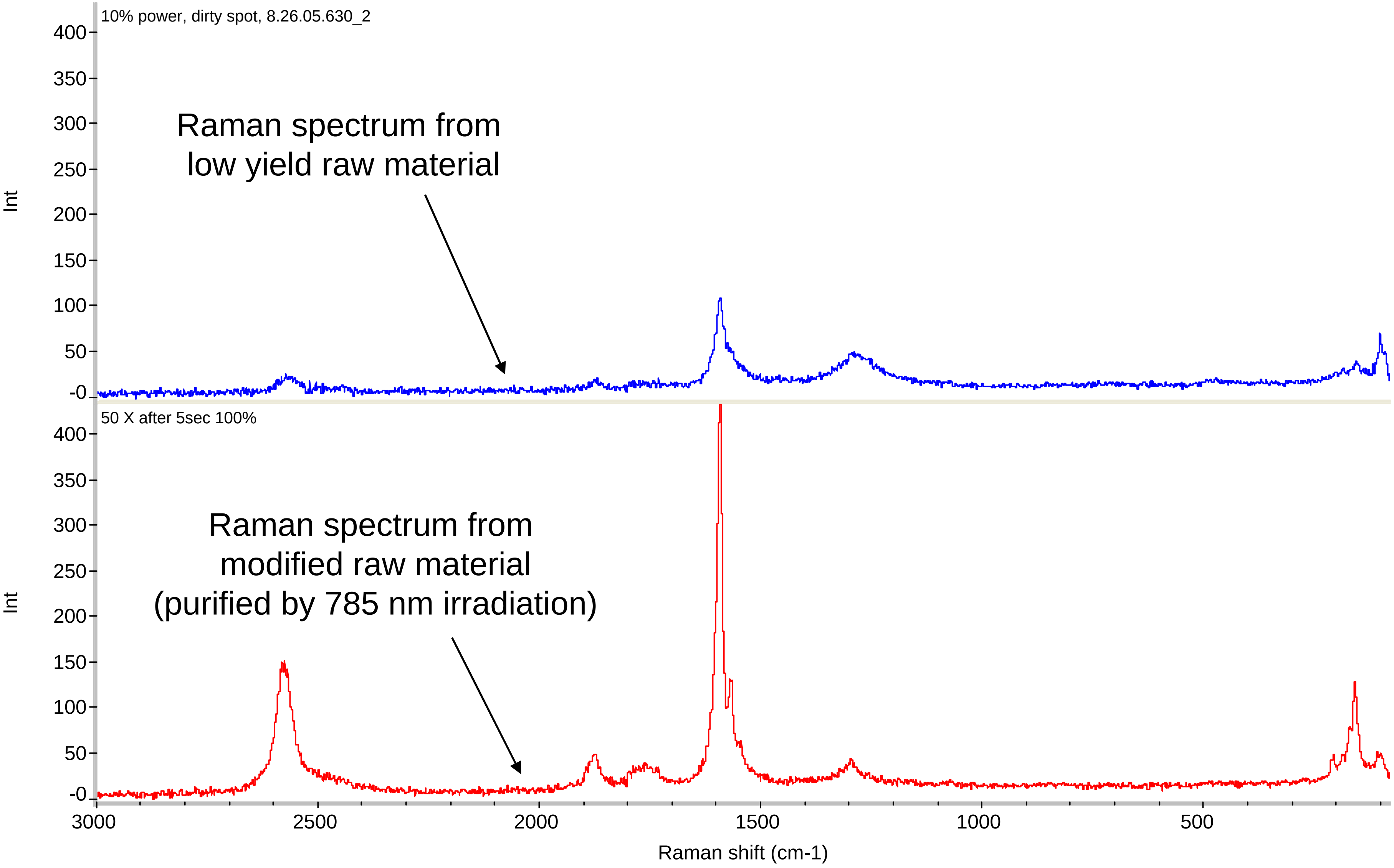
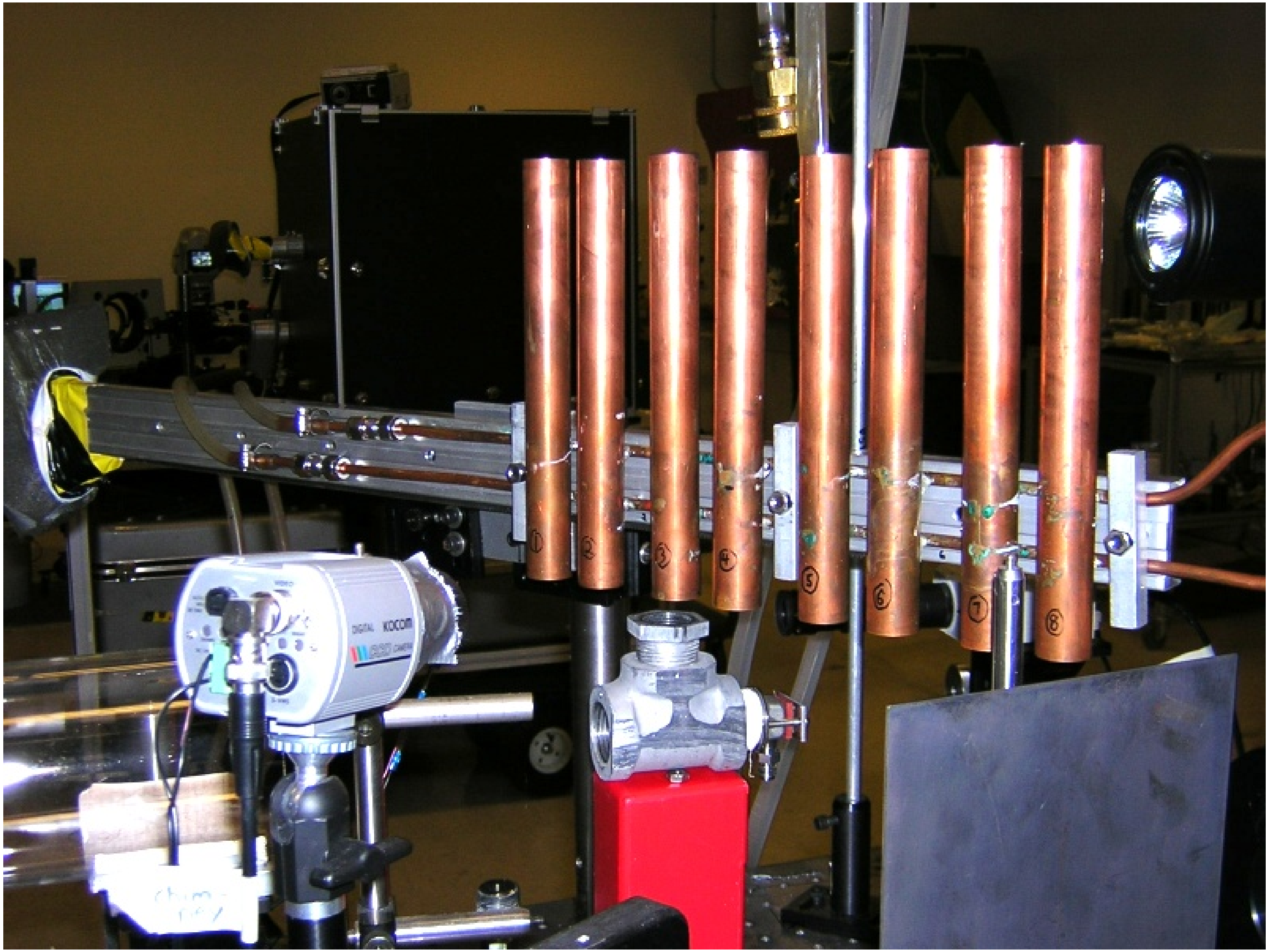


Eight Position Sampling Chimneys Used for Fast Optimization Runs



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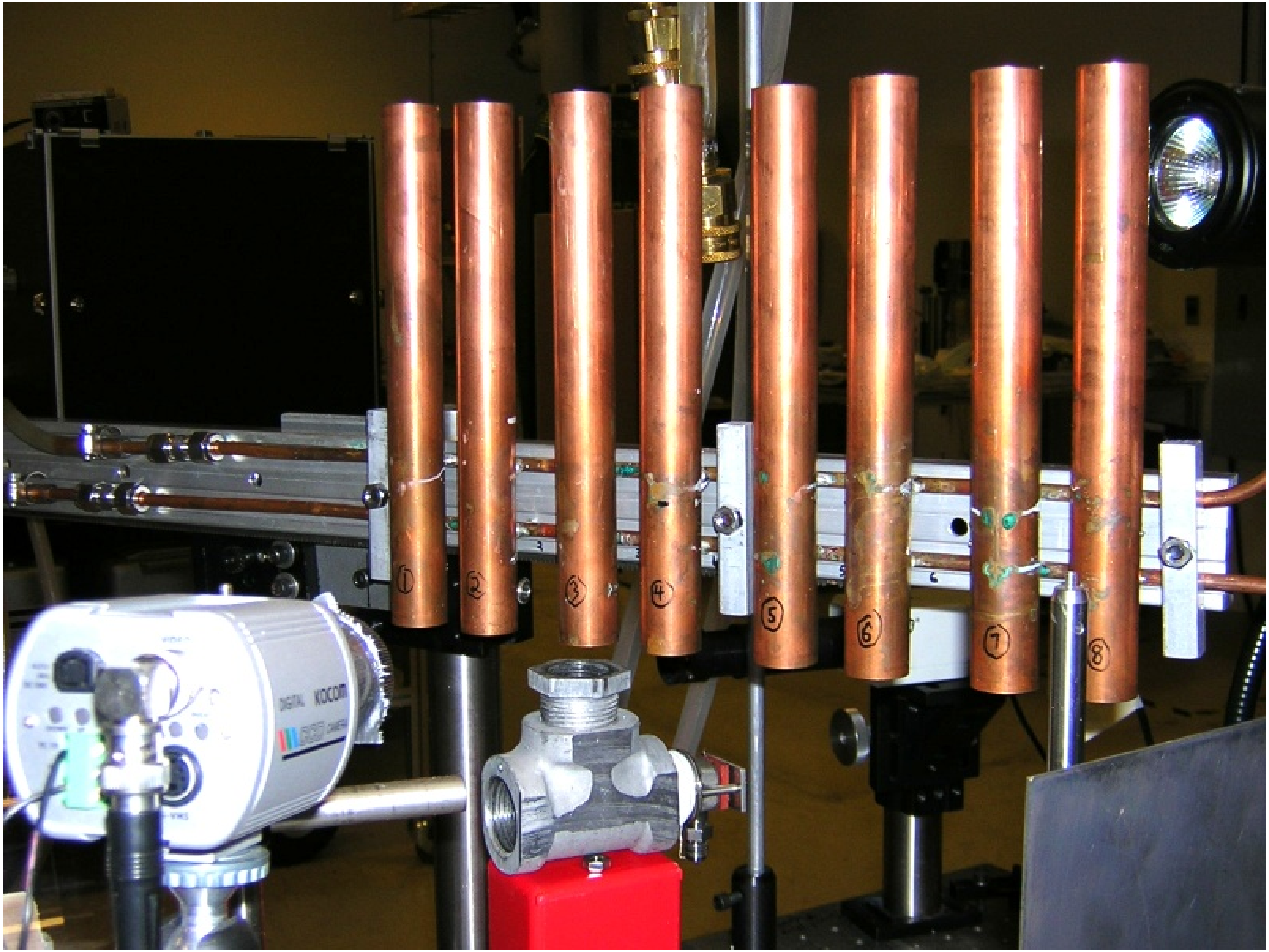
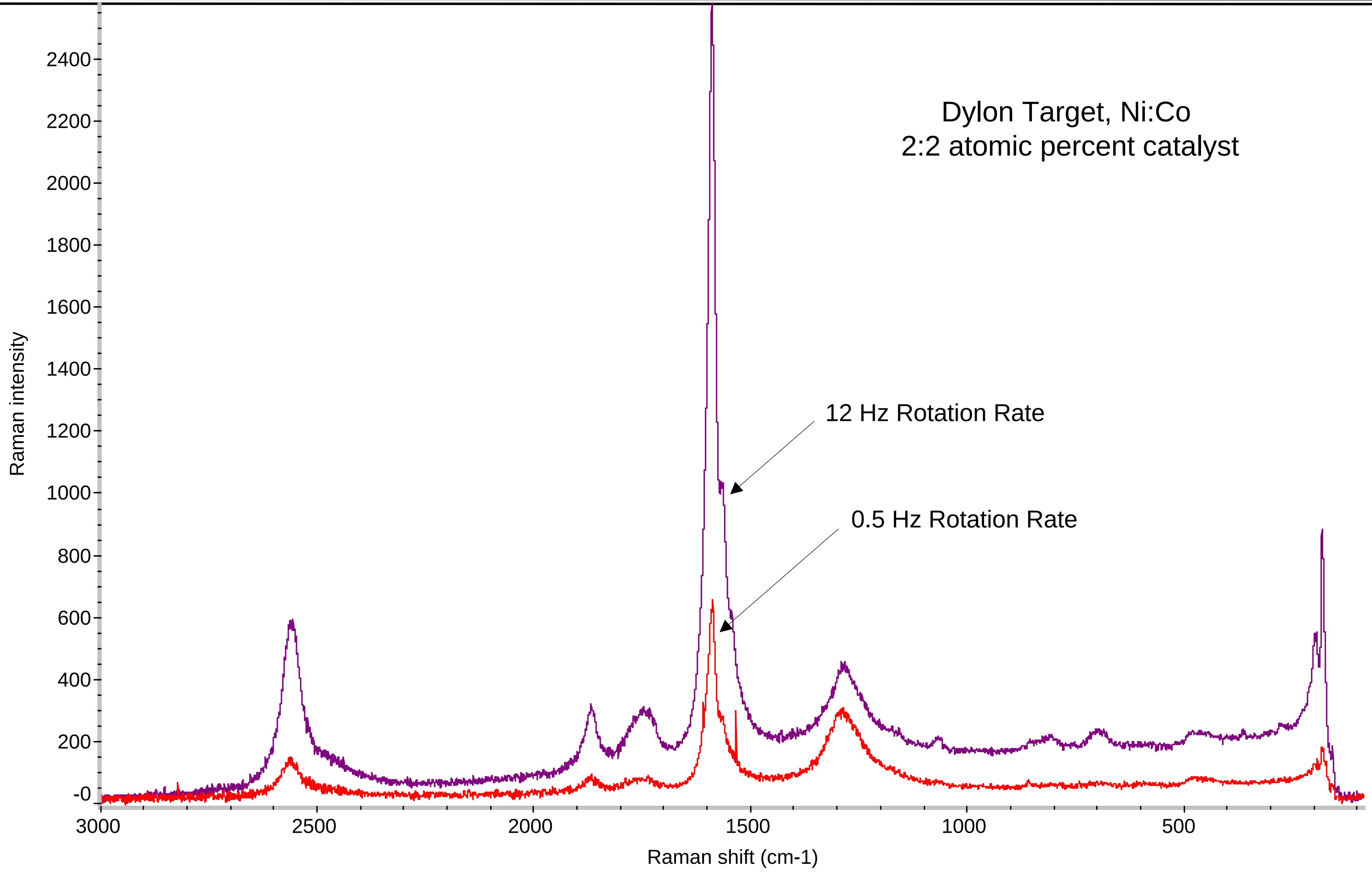
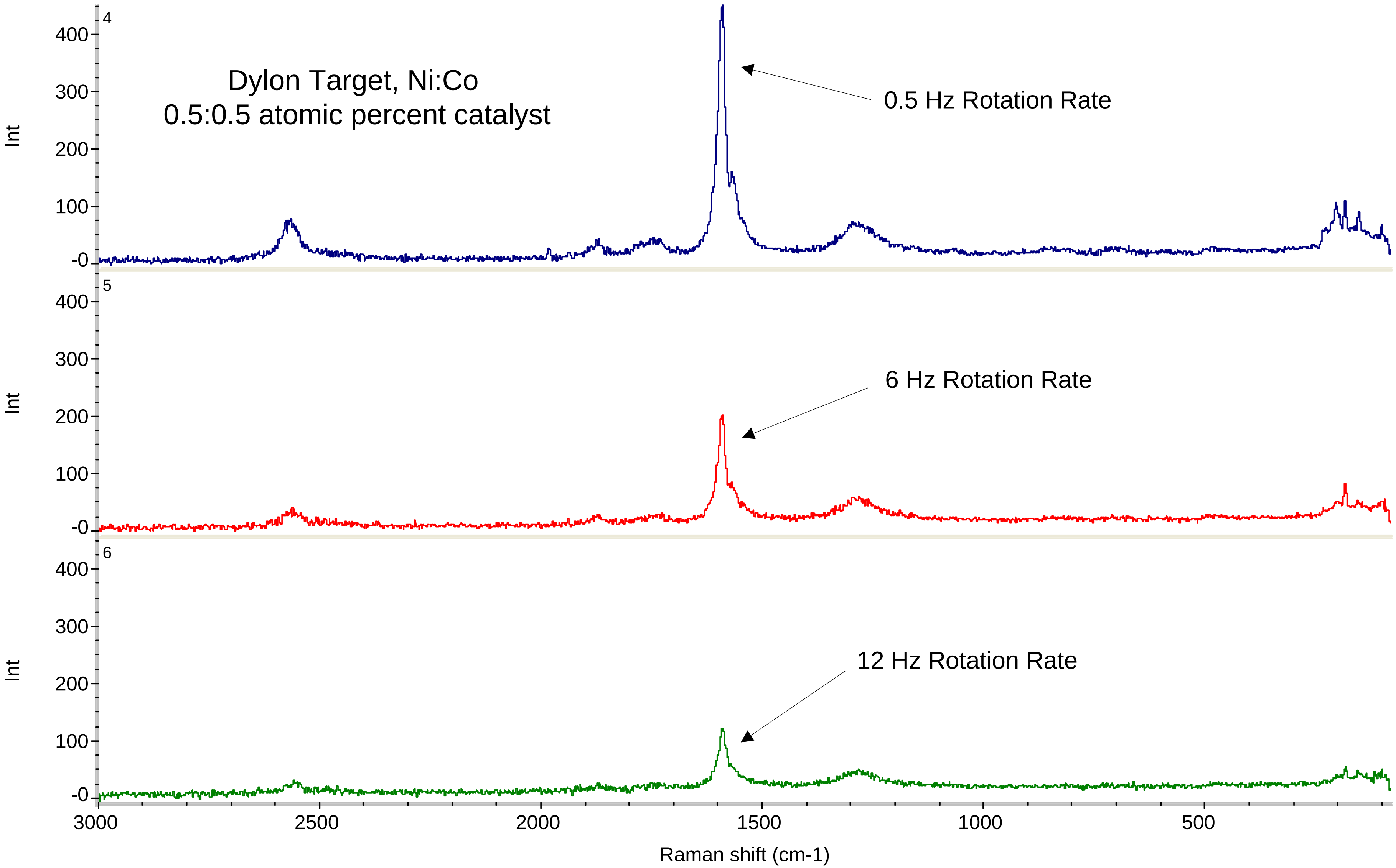


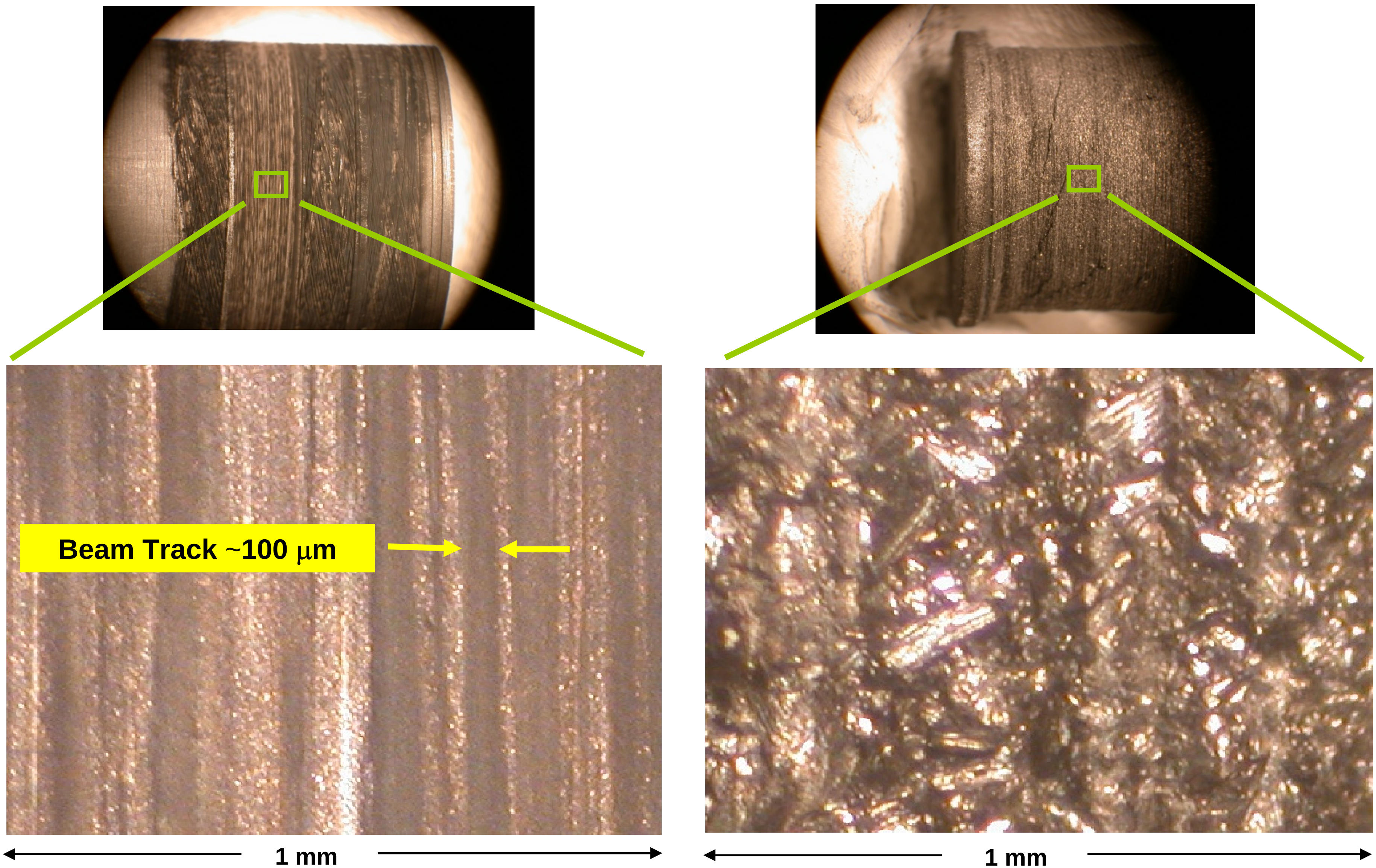
G band Rises with Increasing Spin Rate at High Metal Catalyst Fraction



G band Drops with Increasing Spin Rate at Low Metal Catalyst Fraction



Target Grain, Dylon vs. EDM Graphite
Optical Microscopy of Ablated Surface



SEM/EDS Image of Dylon/Phenolic Resin Target (carbon dark, metal catalyst is light)

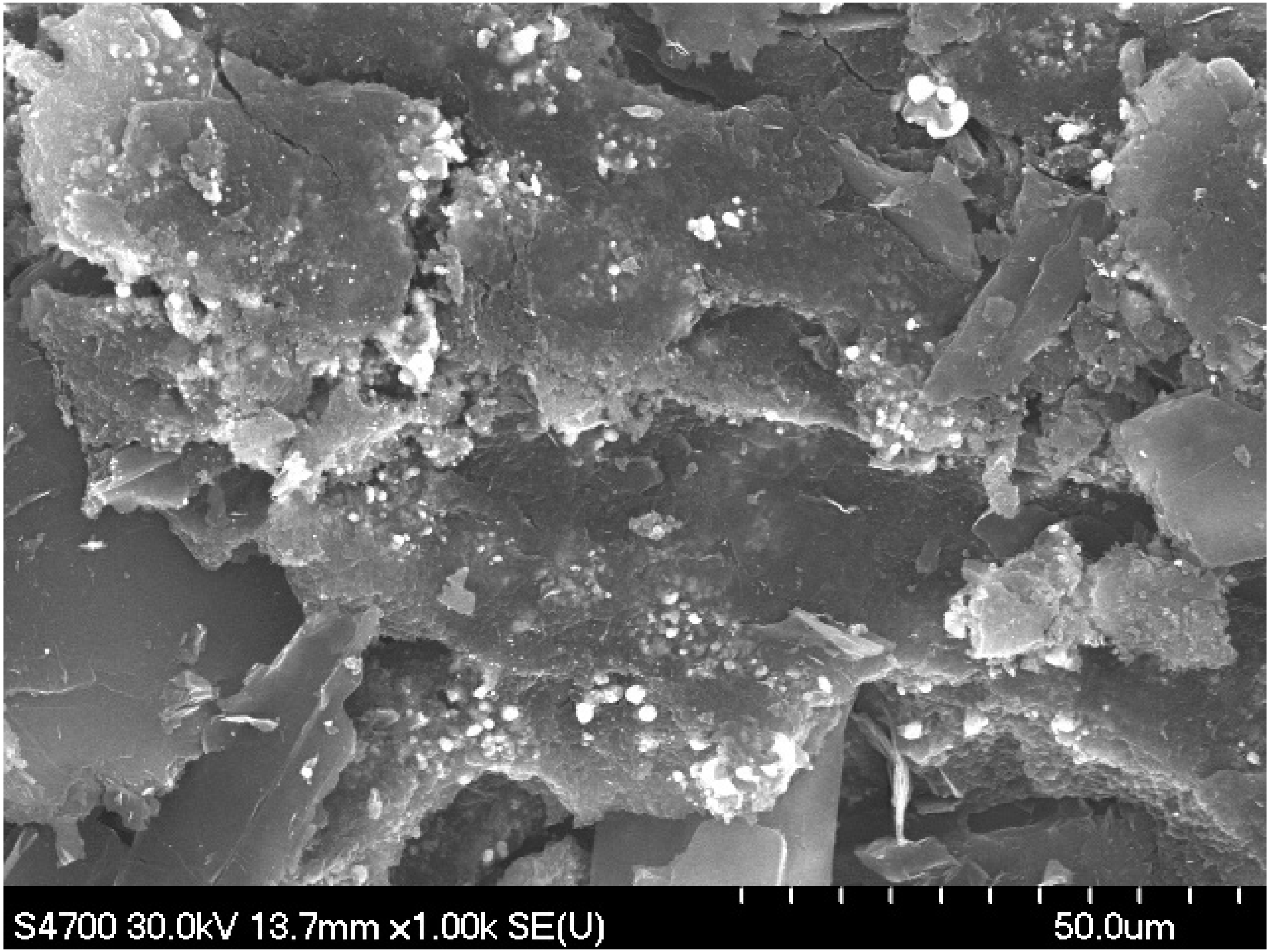


Image Courtesy Jianjun Wang, College of William and Mary

SEM/EDS New, Fine-Grained Target (carbon dark, metal catalyst is light)

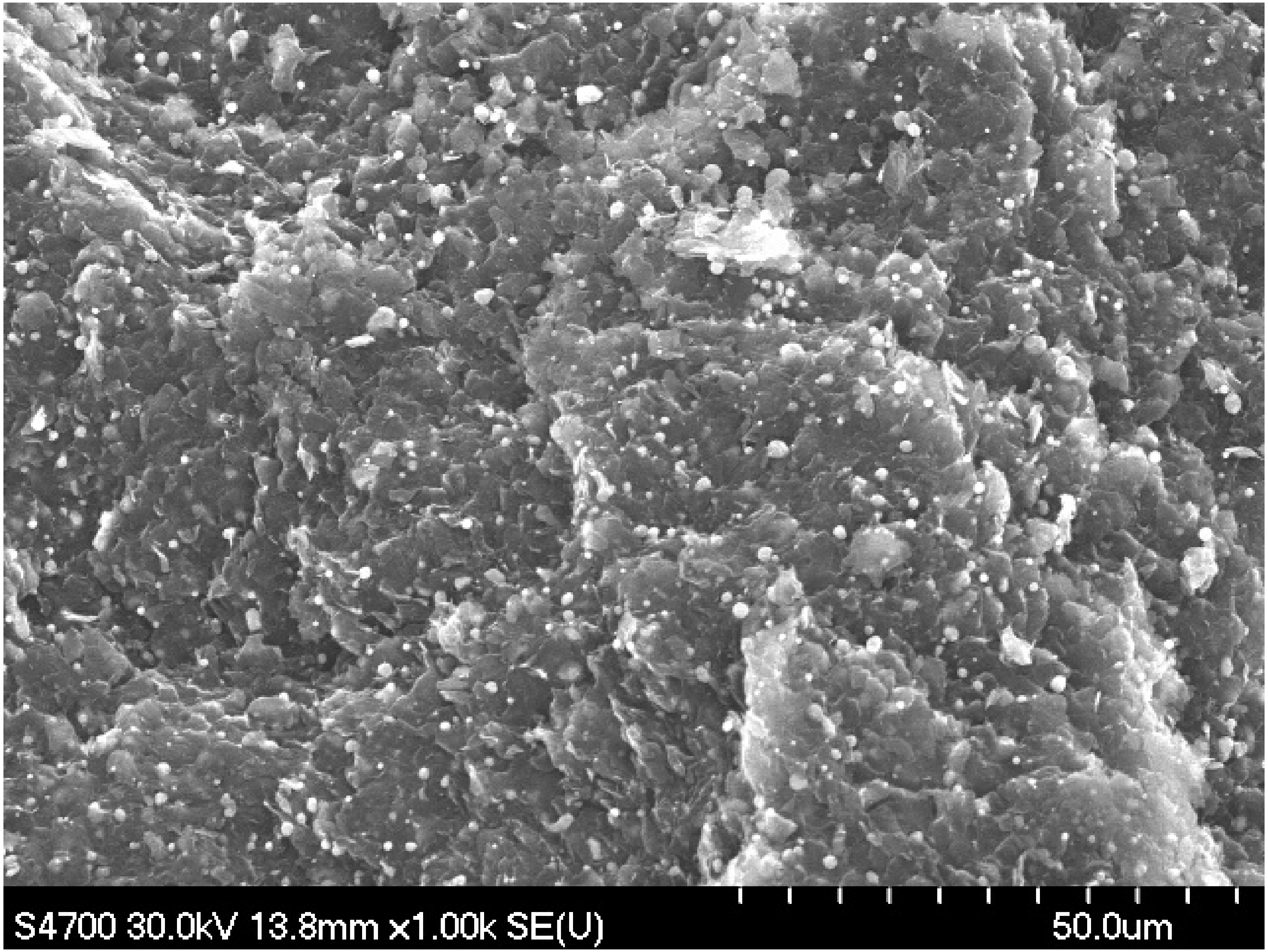
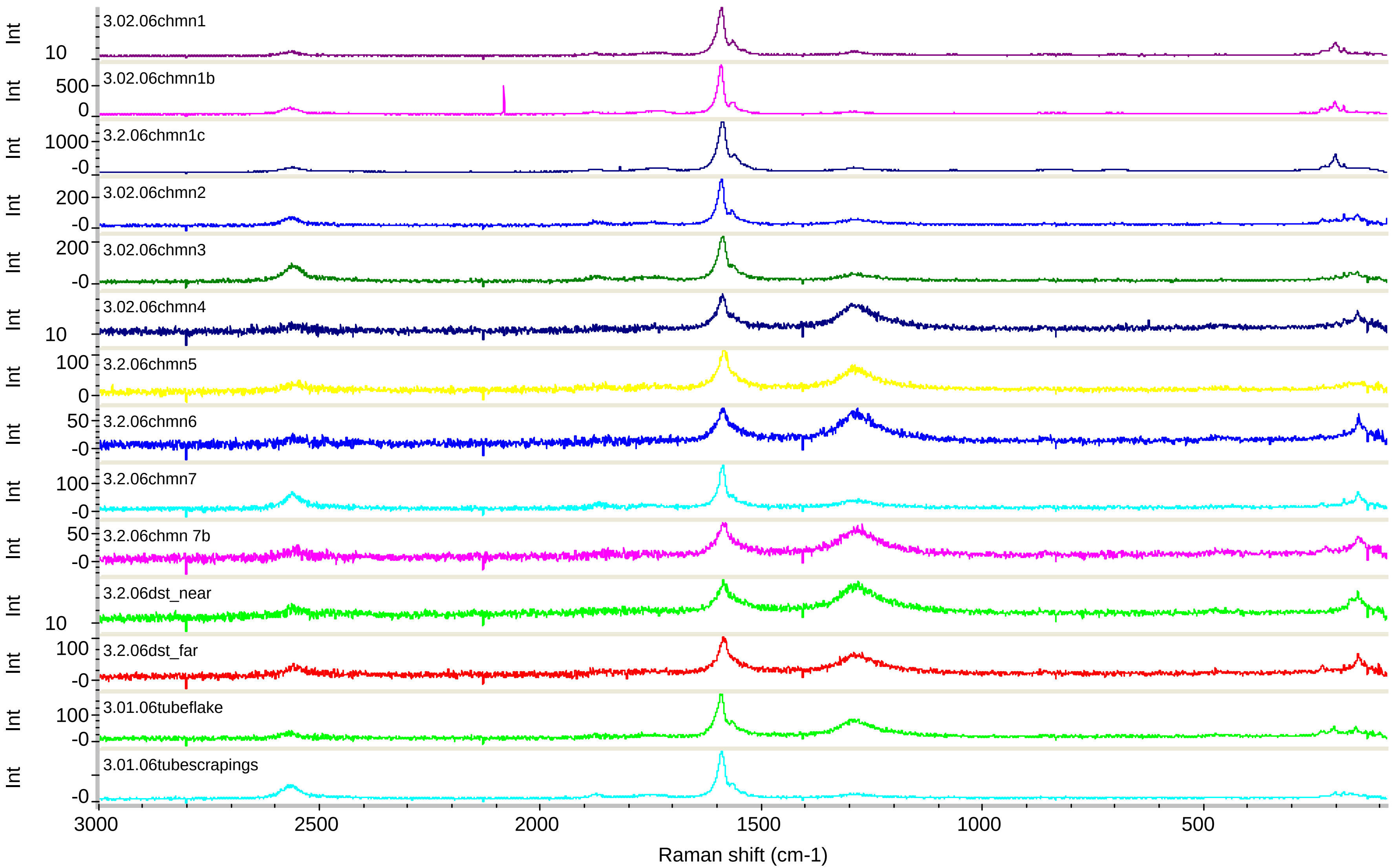
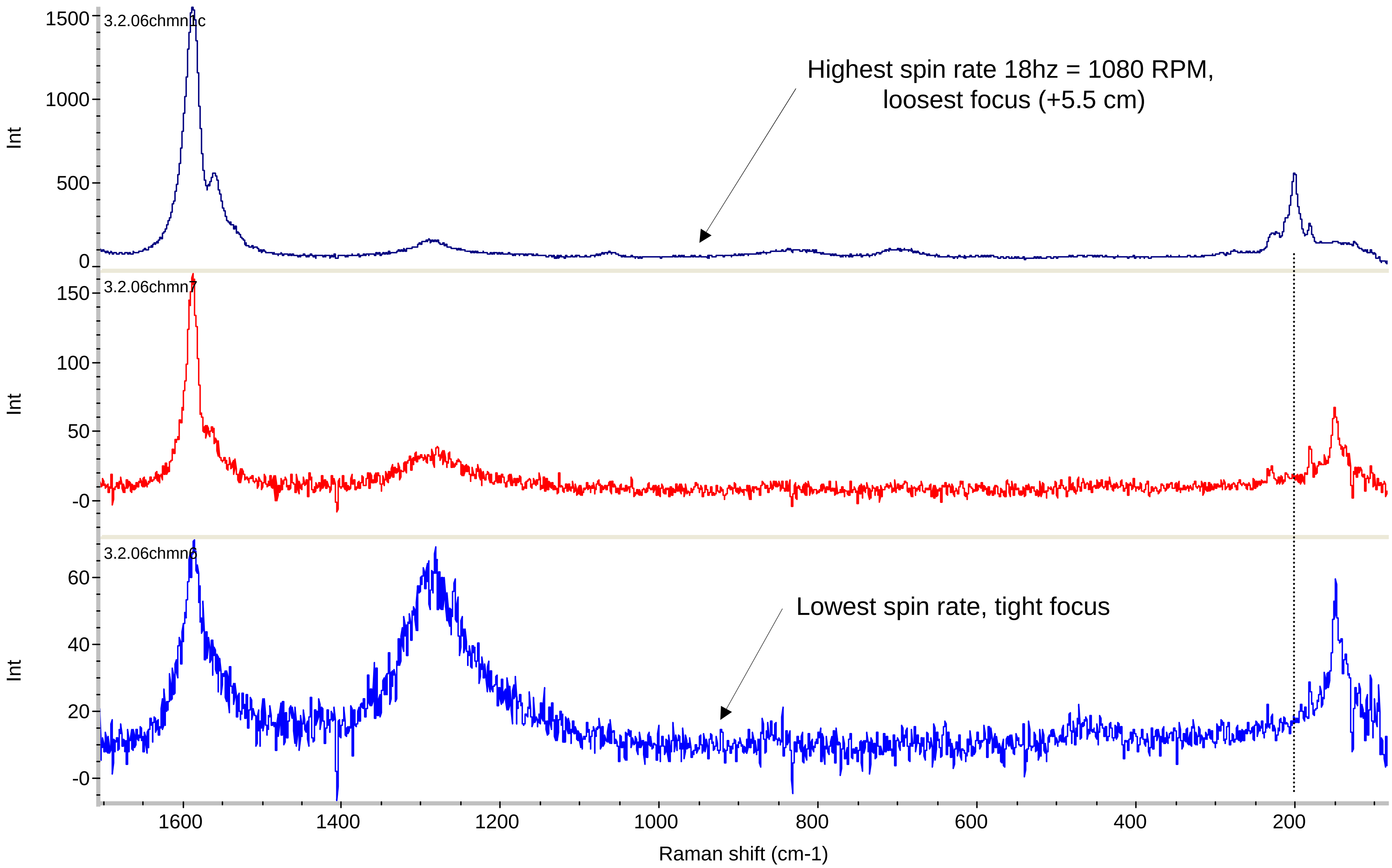


Image Courtesy Jianjun Wang, College of William and Mary

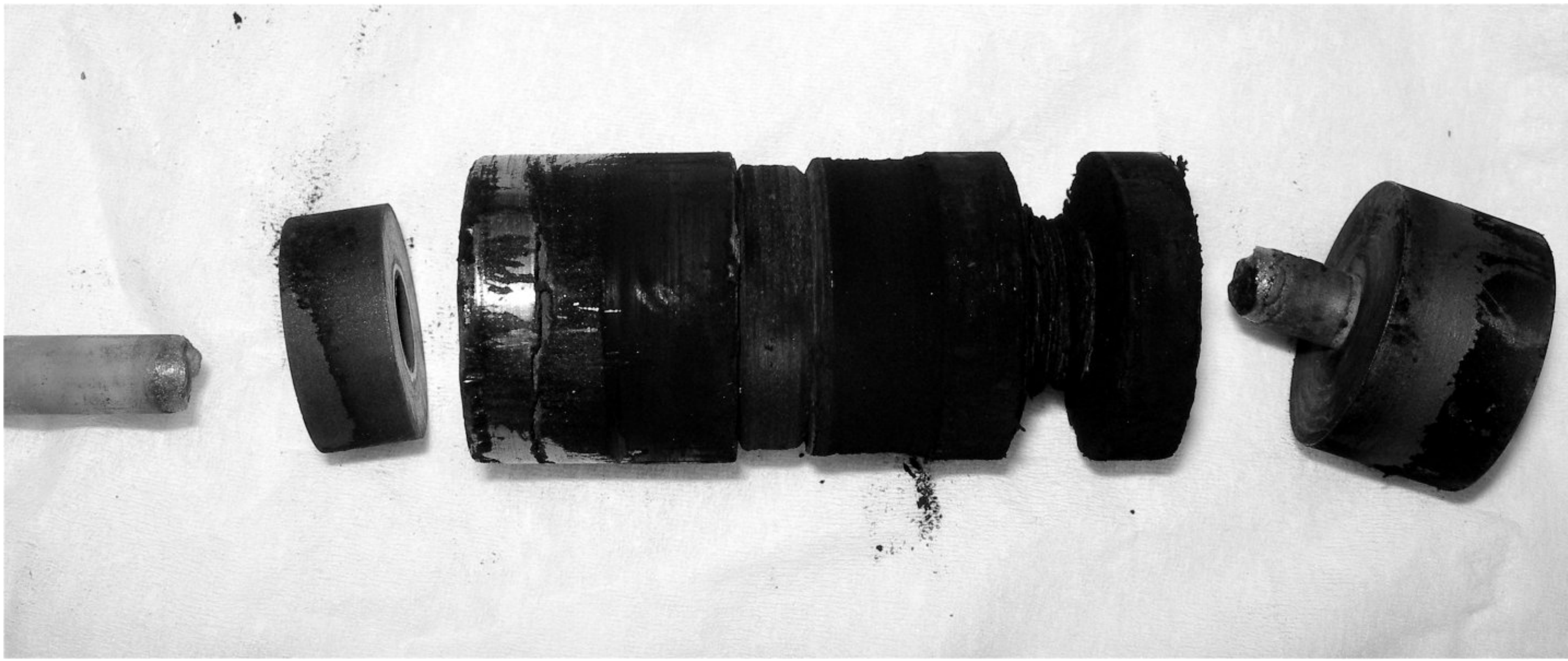
Raman Spectra, March 1-2, 2006



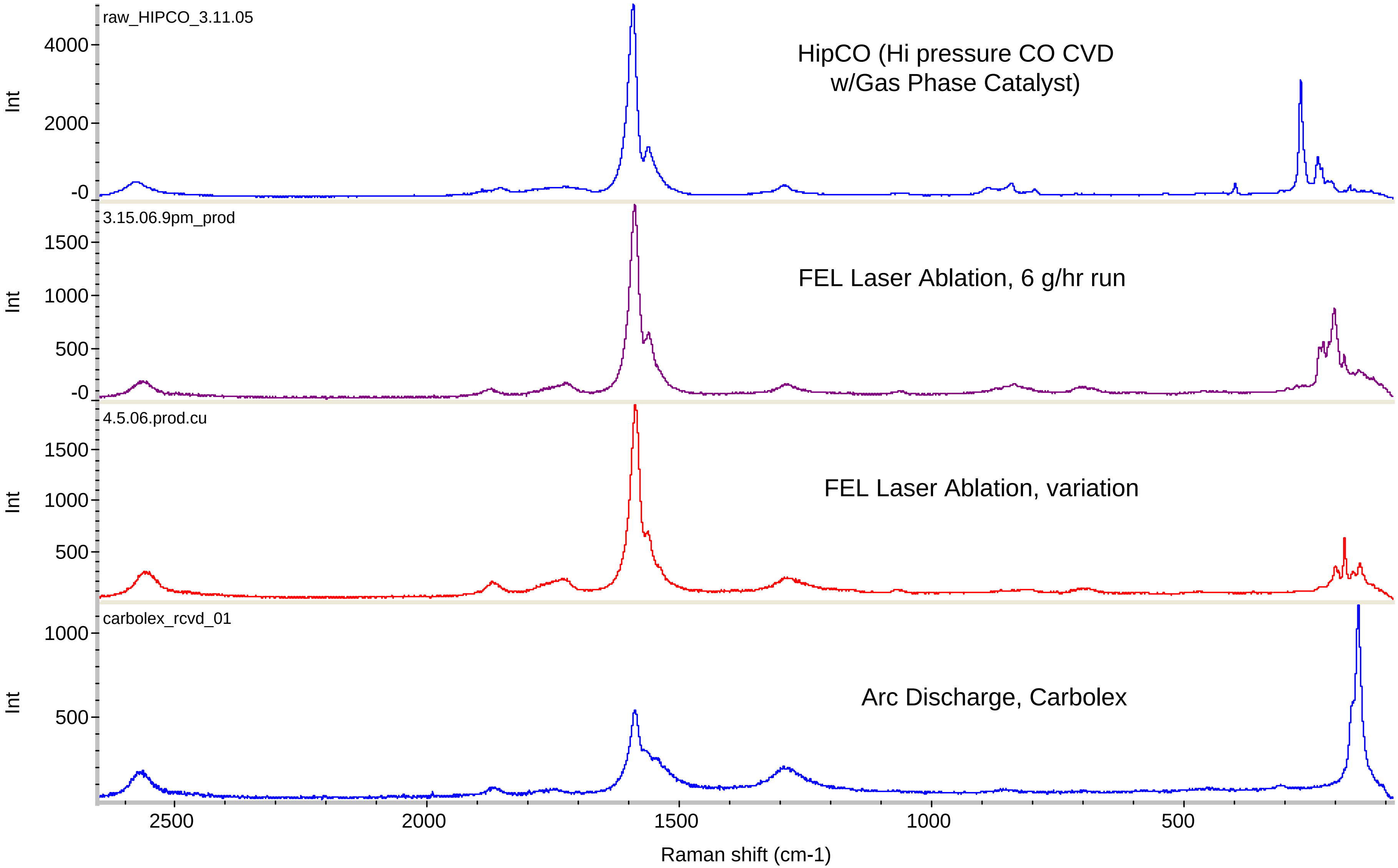
March 2006, Raman Spectra, Chimneys 1,6,7



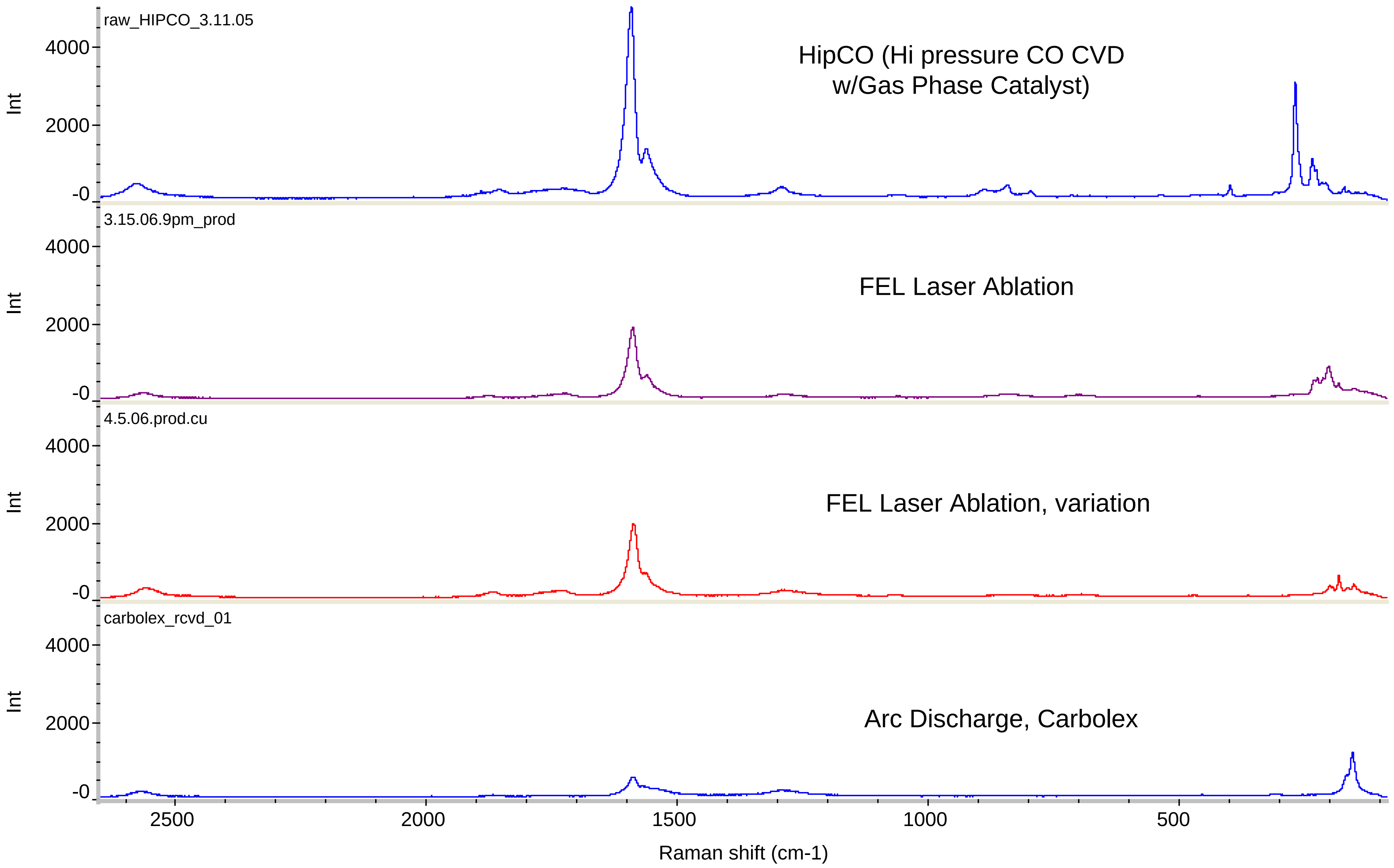
Used Target, March 06, Showing Thermal Damage



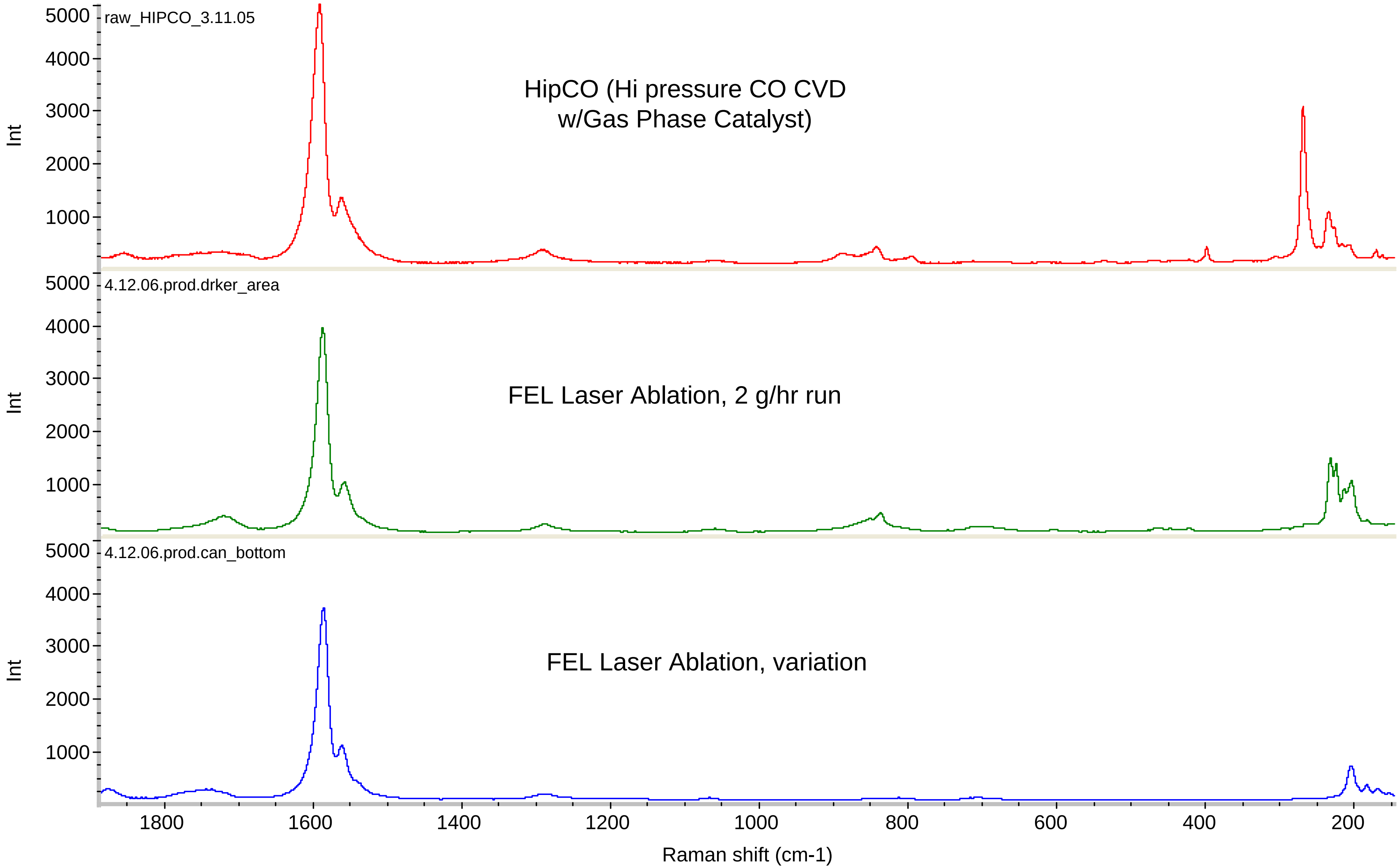
Comparison of FEL Synthesis with Commercial Methods



Comparison of FEL Synthesis with other Commercial Methods (4/5/06)



Latest Comparison of FEL Synthesis with Unpurified HipCO (4/12/06)



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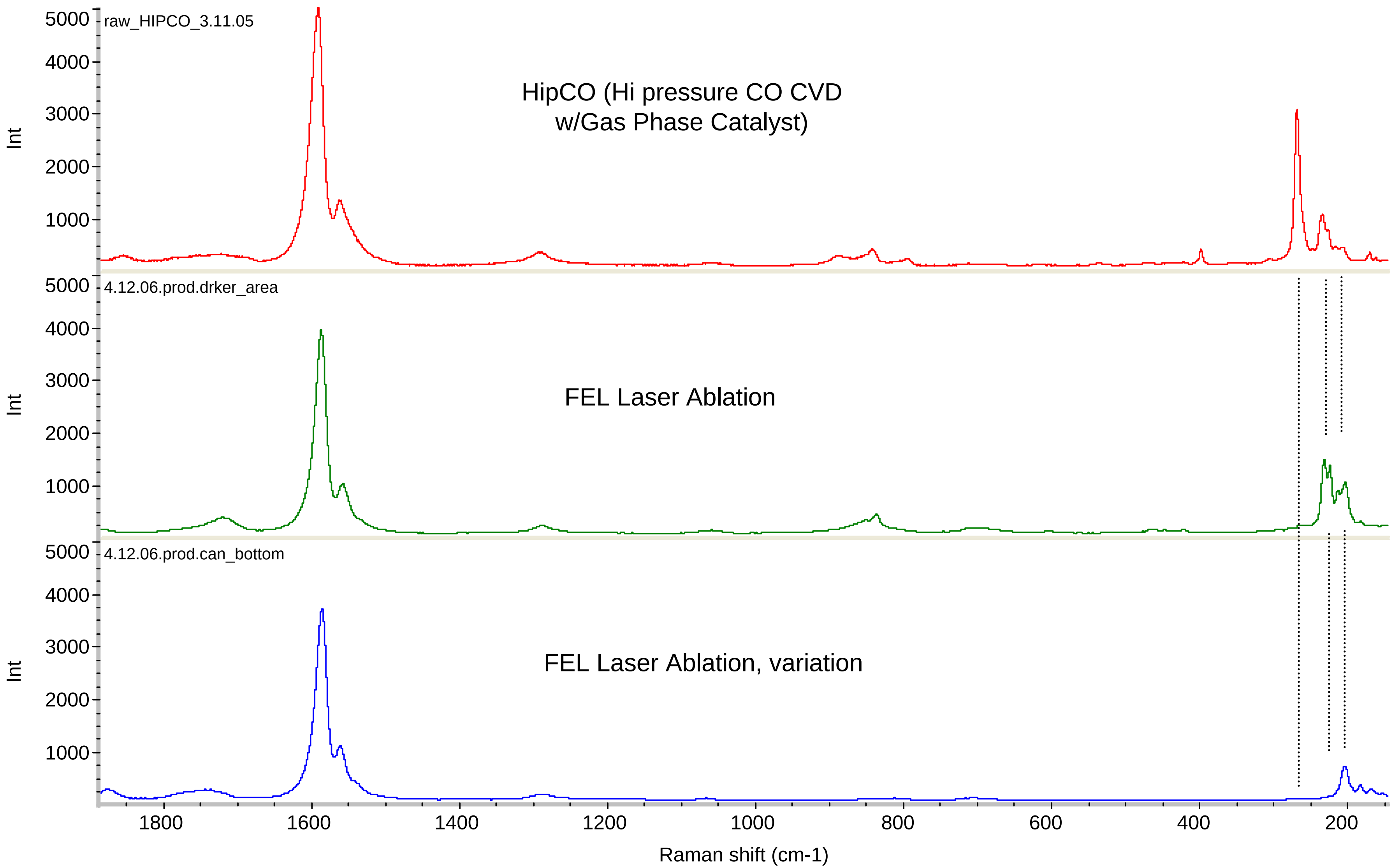
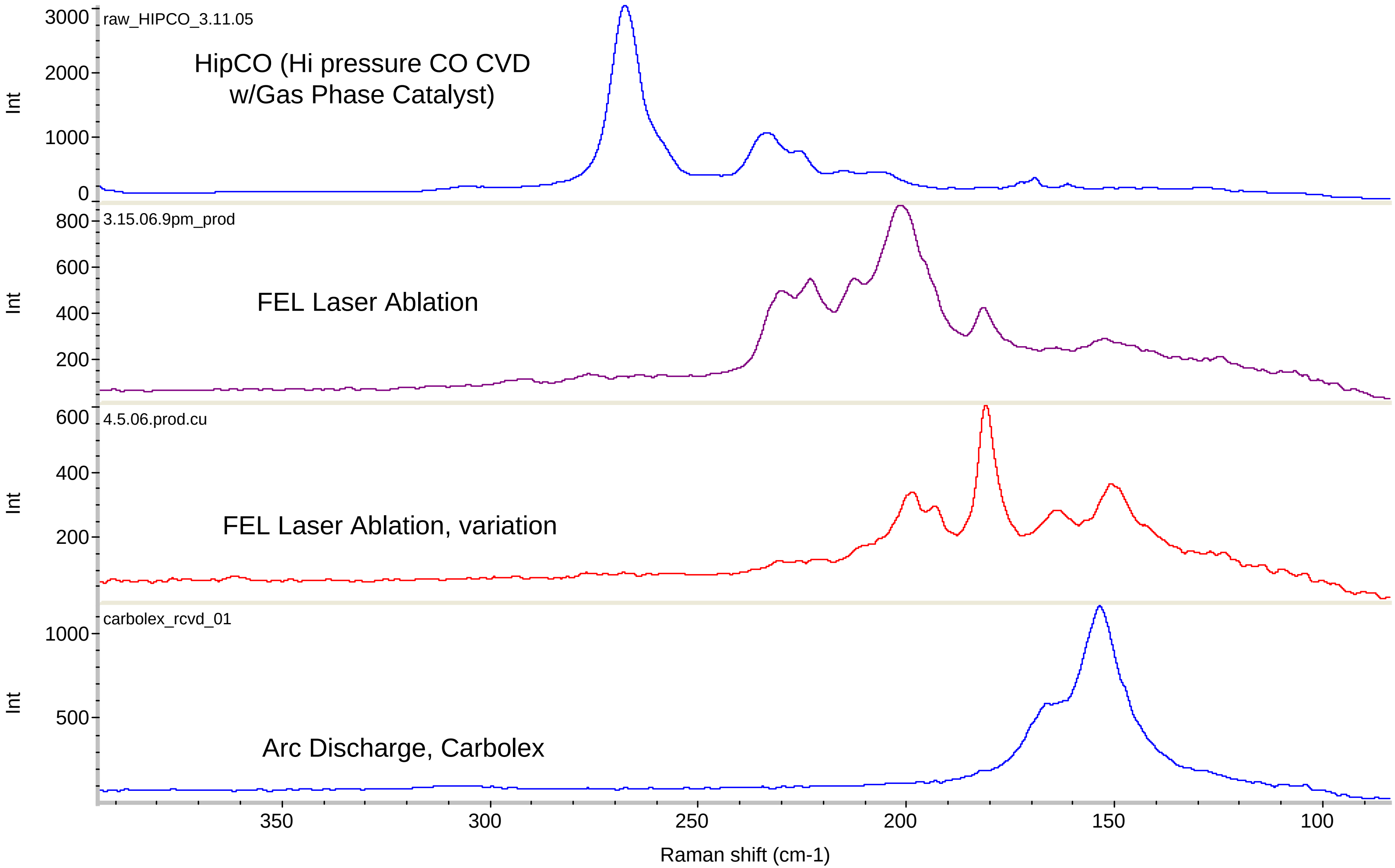
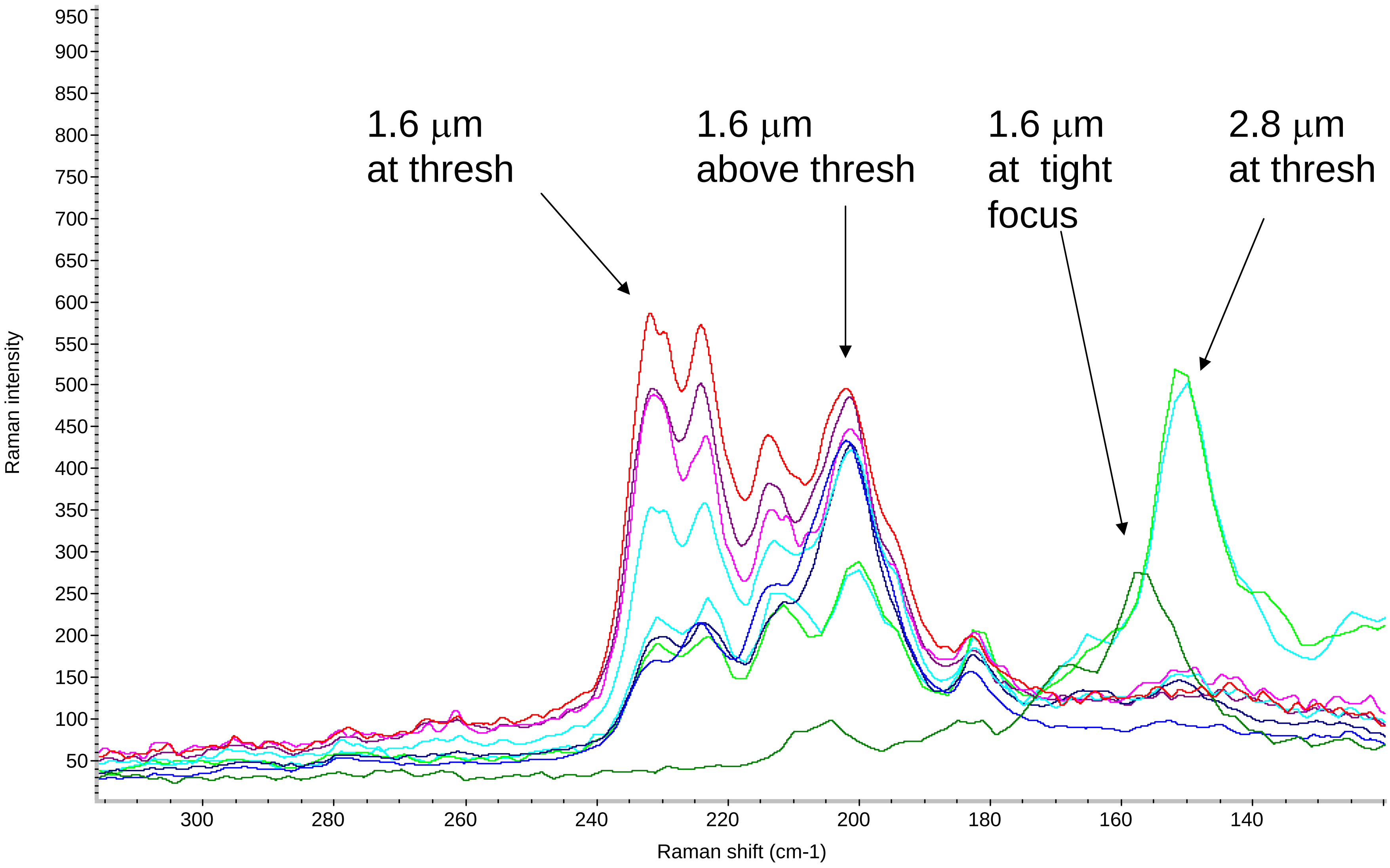


Variability of Radial Breathing Modes Comparison of FEL with other Methods



FEL CNT RBM (tube diameter) Variations with Wavelength and Focusing Condition



Conclusions

Engineering:

Demonstrated high yield, HipCo-level-quality SWNT production at a production rate of 2-10 g/hour (10 to 50 X HipCo or Nd:YAG synthesis rates) at ~750 W average power, at 1.6 micron.

Developed specialized fine-grain FEL CNT target made in-house for < $10/lb.

Developed RF-heated laser oven apparatus (flow geometry, heat transfer/temperature distributions, target holder, production and sampling collectors, scanning and other remote controls, and visualization).

Physics:

Found that the highest average yield is always at “incipient extinction” (the largest laser spot size before the plasma goes out.)

Found that the highest yield flakes of raw material always contain the smallest diameter tubes (the “smoking gun” pointing to ultrafast ablation effects).

Showed that RBM (tube diameter) varies with laser condition at a given wavelength as well as with wavelength.

Future

Production at 750 W quasi cw is now routine, and will continue as required, but main focus will be on scale-up with:

Shorter Wavelengths and Higher Power (and more temporal stability)!

Projections?

At least 20-40 g/hour of highest grade material, ~5 times more for lesser grades (straight linear extrapolation).

“Designer” tubes with selectable diameter. (length?, chirality?)

More access to higher quality tubes with more choice regarding important properties => real progress in applications.