DE-FE0031794

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Virtual Review: 27 April 2021, Time: 1400

Proposal Title "**Conversion of Domestic US Coal into Exceedingly High-Quality Graphene**"

Main deliverable: Convert a US Coal Product Into 1 kg of Graphene Per Day

Project/Grant Period: 10/01/2019 through 9/30/2020

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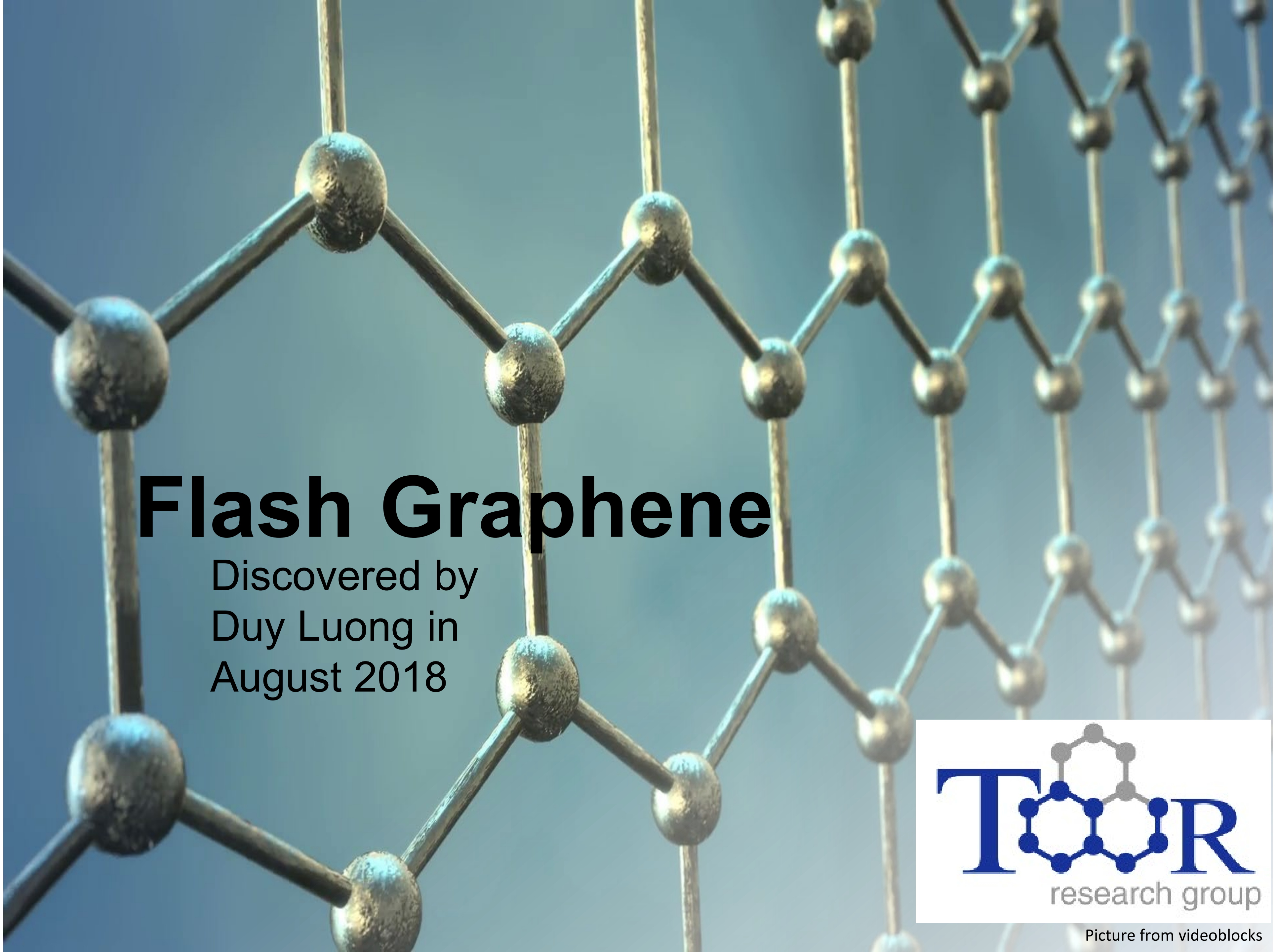
Flash Graphene

Discovered by
Duy Luong in
August 2018



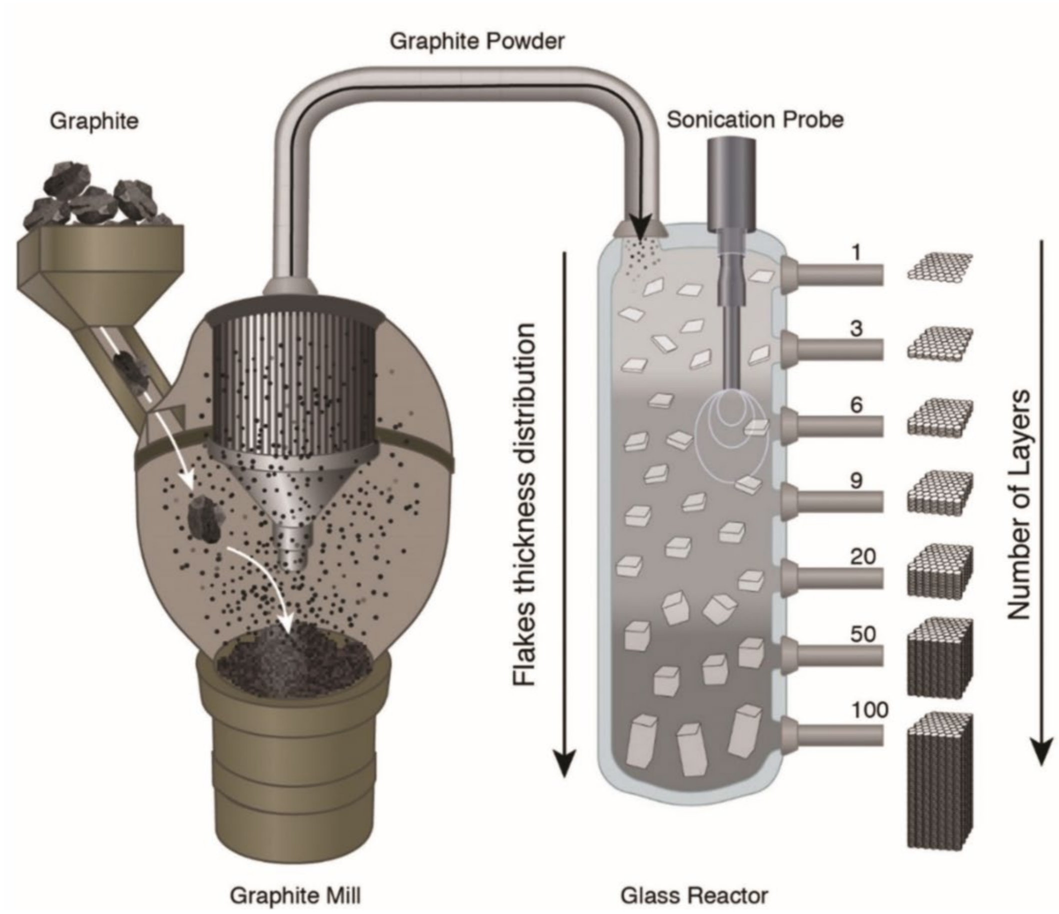
Picture from videoblocks

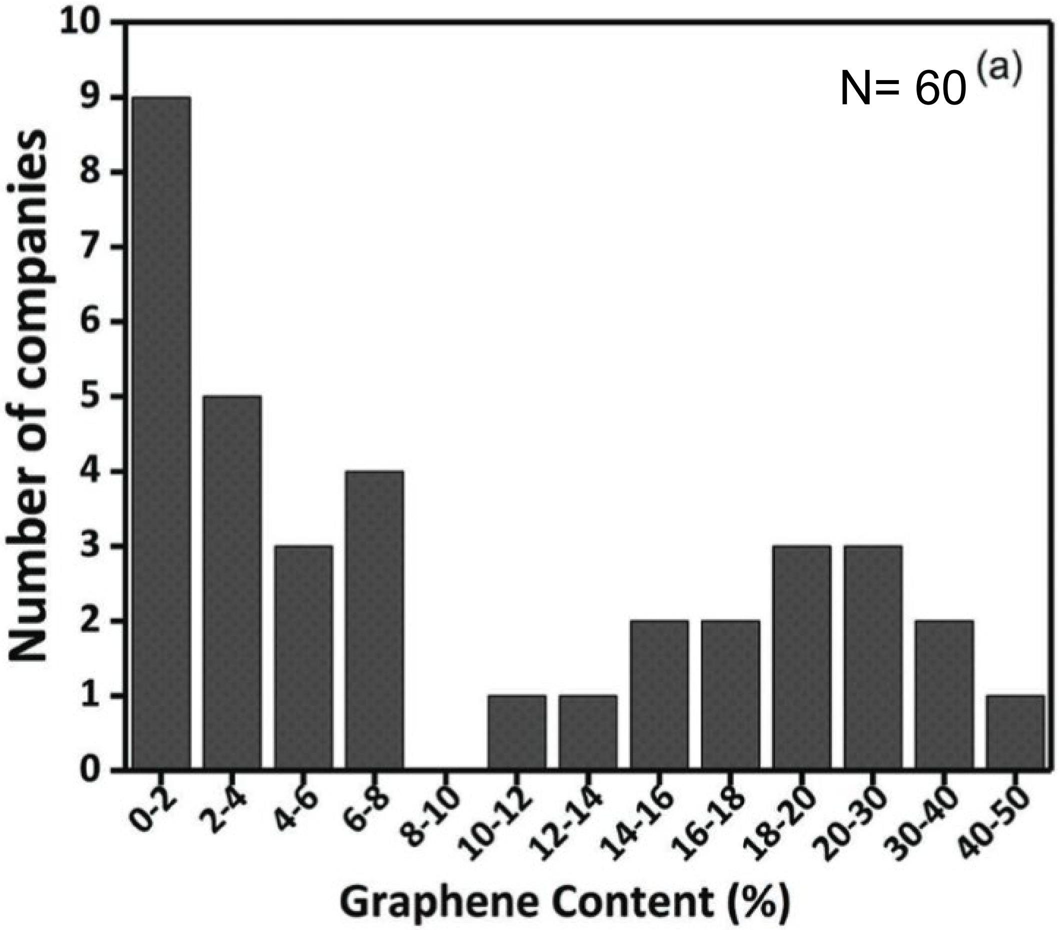
Advantages of graphene

Graphene is:

- nontoxic and even used in several medical applications;
- is naturally occurring in the environment and agglomerates are the natural mineral graphite;
- is a terminal natural sink for carbon since microbial decomposition is on the order of hundreds of years, if at all, so it never again enters the carbon cycle (i.e. graphite’s geological stability);
- can be used in composites of all types including plastics, which can be re-flashed at end of life to make fresh graphene. So there are extreme energy savings in lessening of the downstream composite hosts;
- At the current price of graphene being $60,000 to $200,000 per ton, there is much room to capture markets;
- The electrical flashing cost is estimated to be $35 per metric ton of coal to graphene conversion

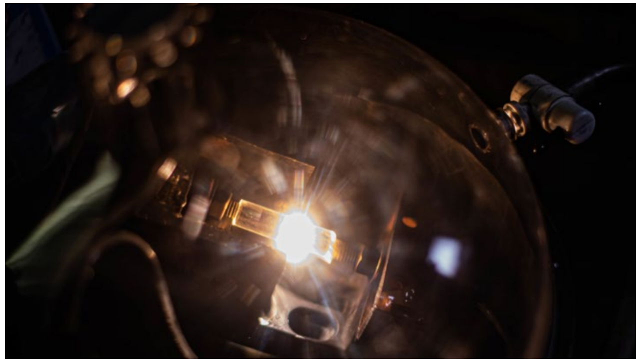
Graphene produced commercially is low in quality

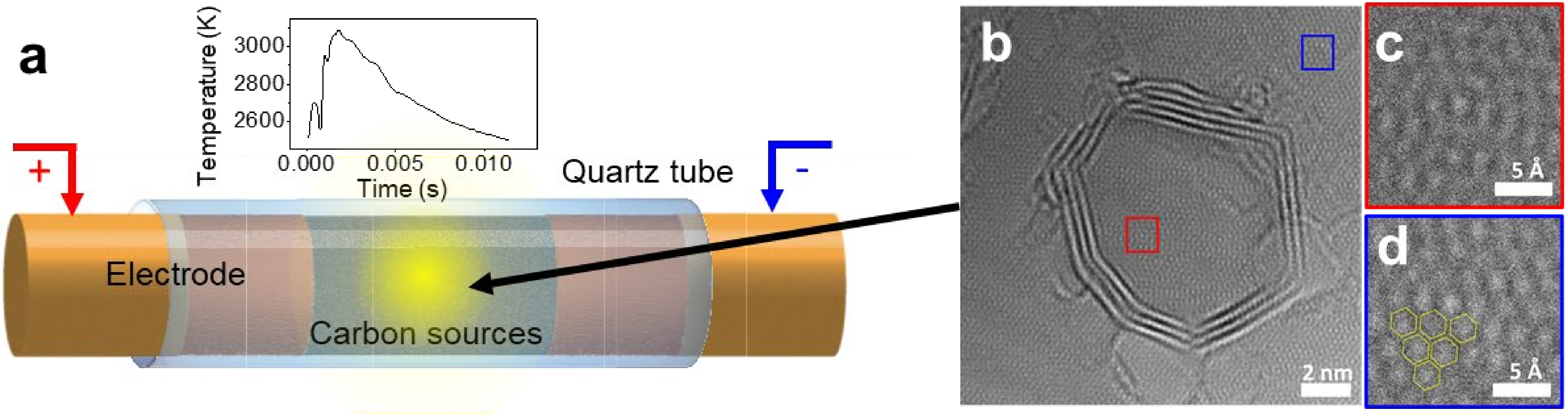




Kauling, A. et al. *Adv. Mater.* **2018**, 30, 1803784.

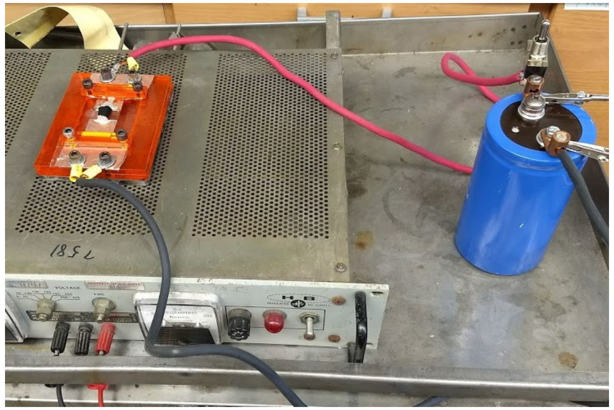
Flash Graphene Synthesis



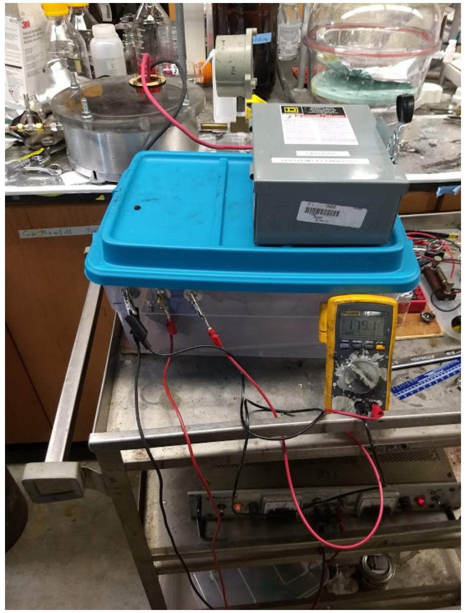


Carbon materials are converted efficiently into high quality turbostratic graphene

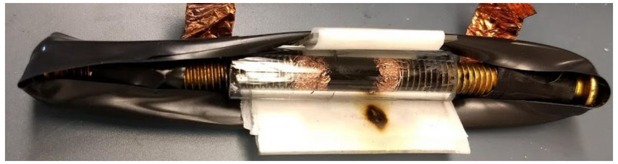
Flash Unit Progression



FJH Beta



FJH V0

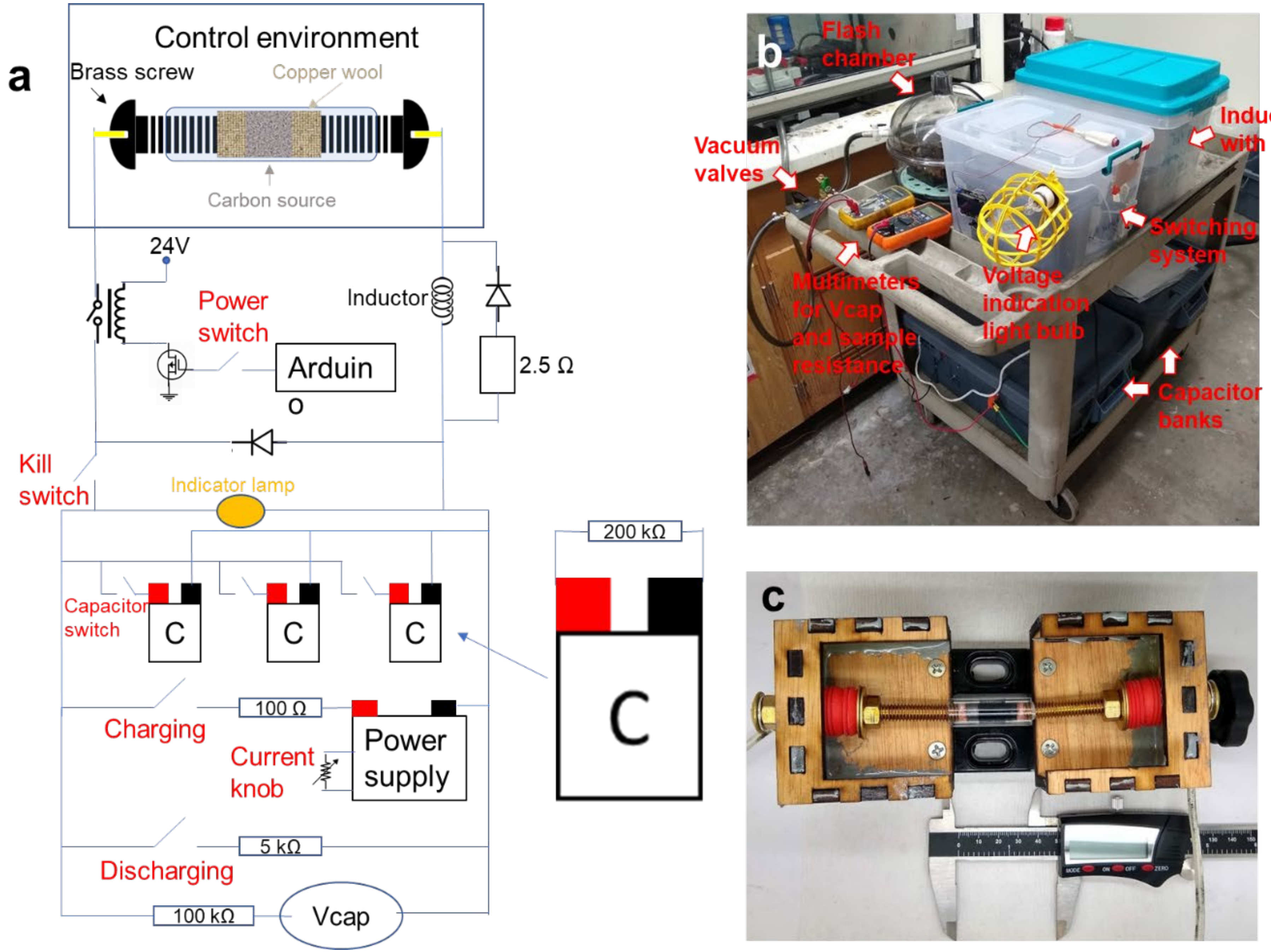


FJH V0 sample

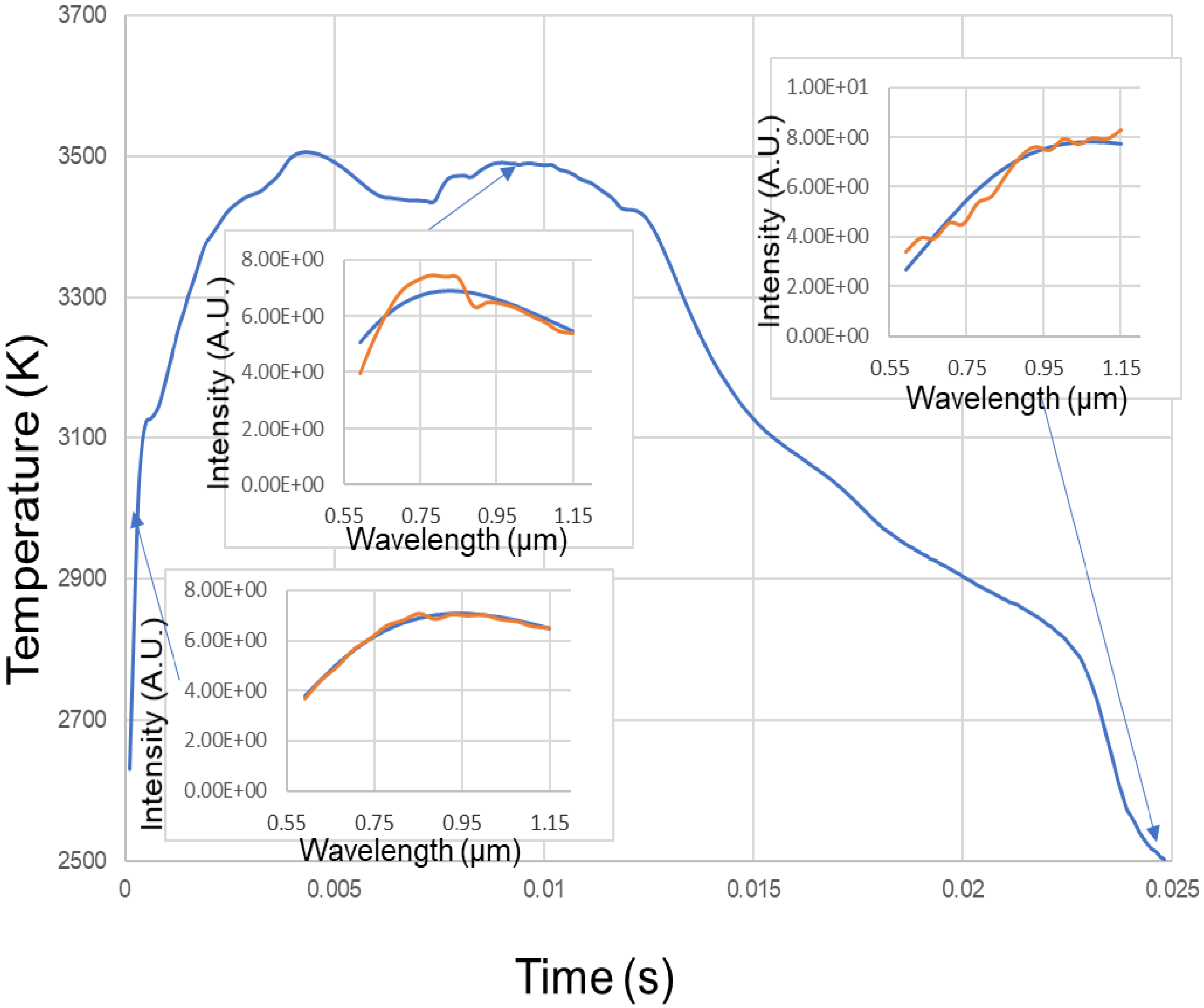
FJH V1

FJH V1 sample

FJH V2.1

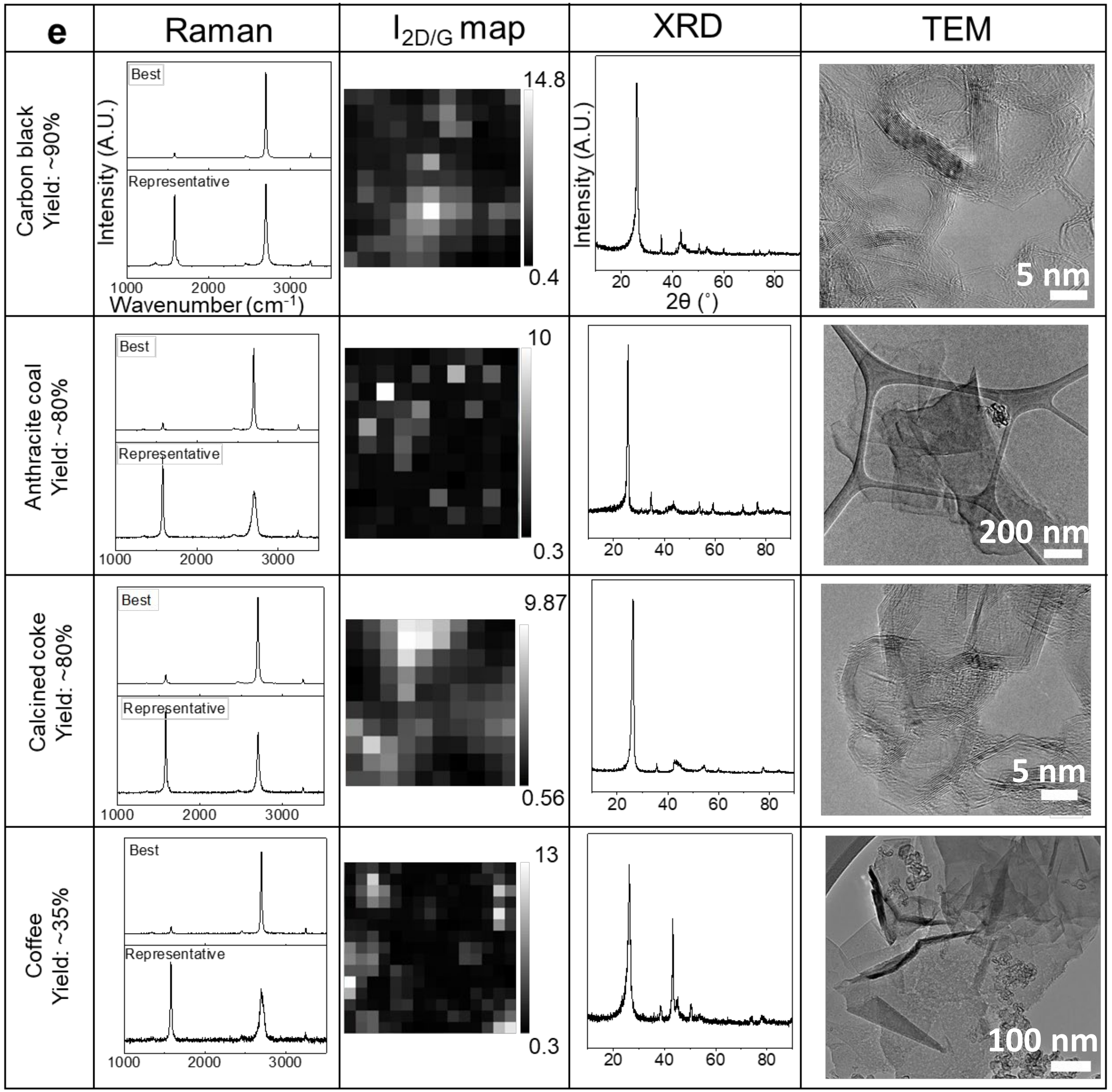


Flash Graphene Apparatus



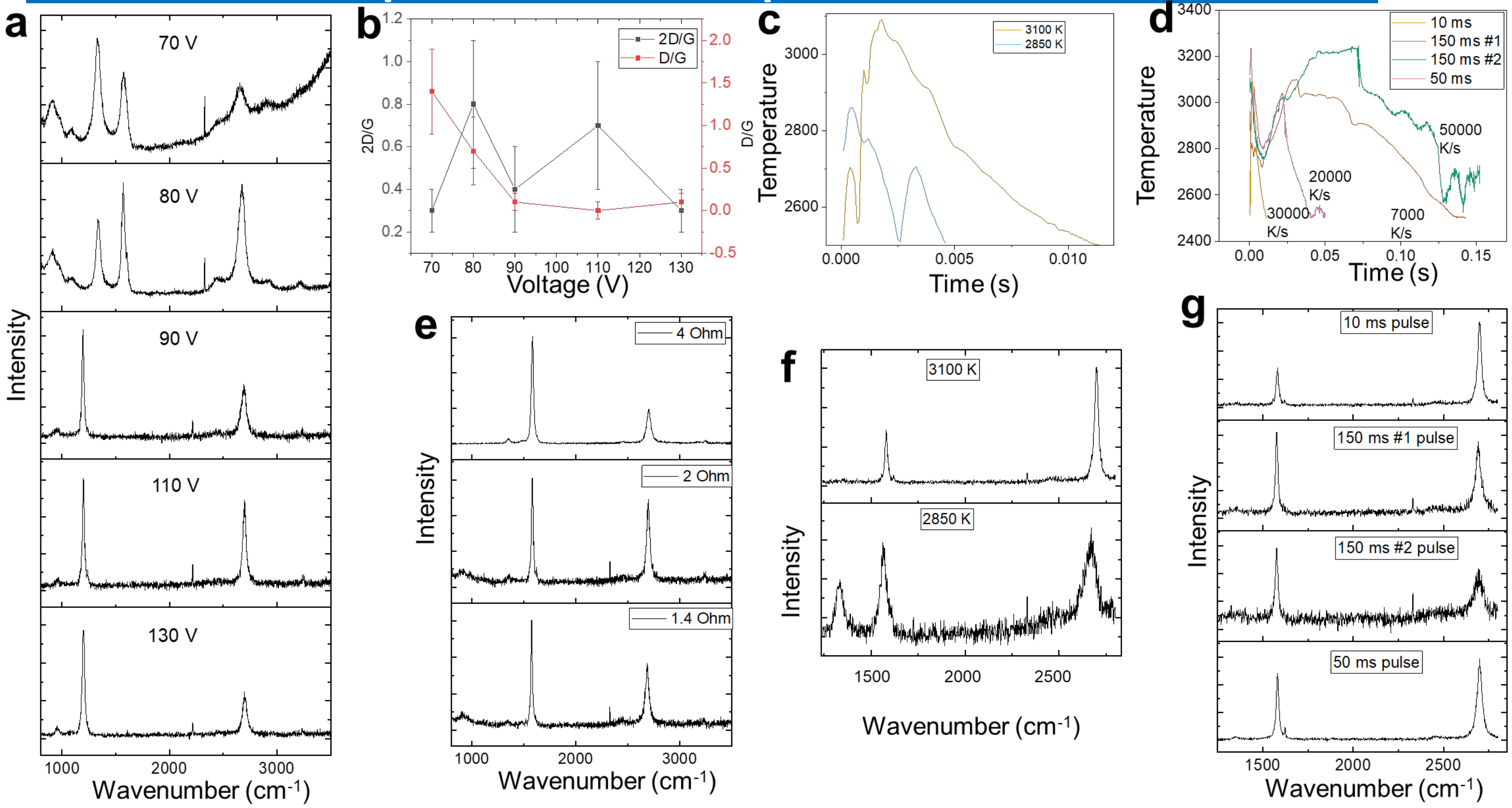
Black body radiation fitting. The temperature from each point of the temperature *vs* time graph is determined by the black body radiation fitting of the spectrum from 0.6-1.1 μm emission. Inset is spectrum fitting for 3000 K, 3500 K and 2500 K.

Flash Graphene Characterization



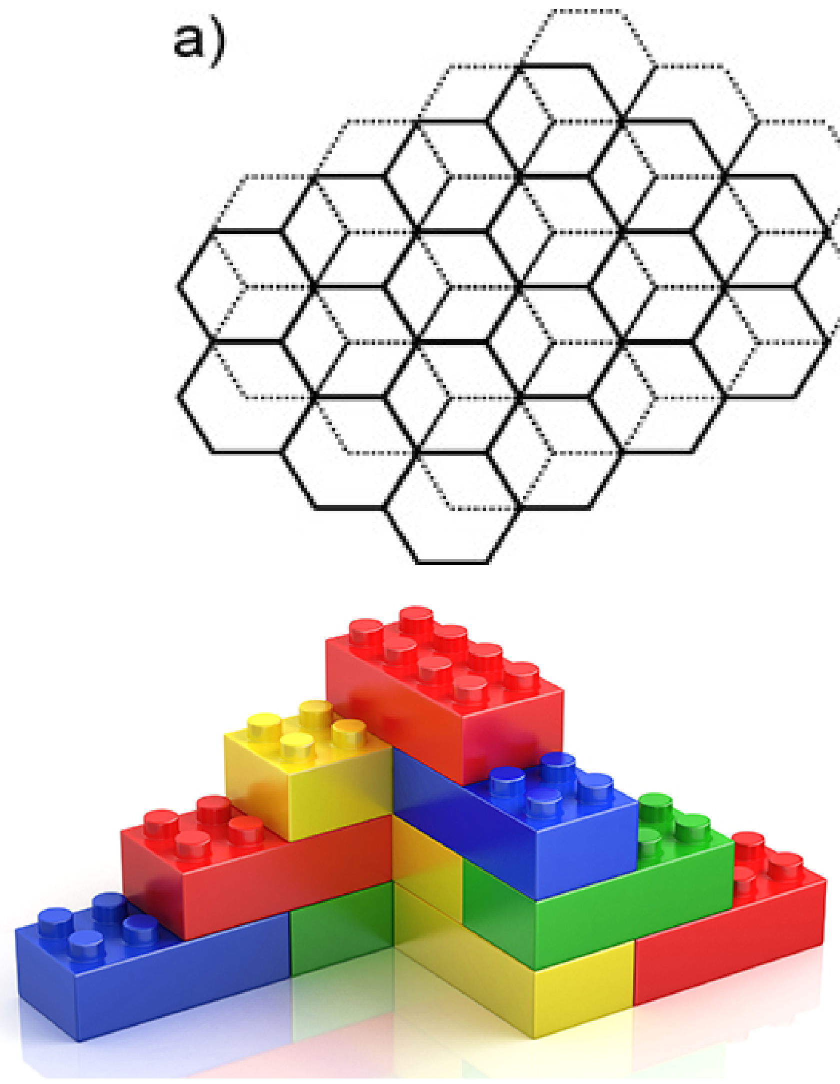
- Various carbon materials can be converted into graphene.
- Graphene quality is high.
- Graphene is turbostratic which facilitates dispersion in composites
- $35/ton in electrical energy costs

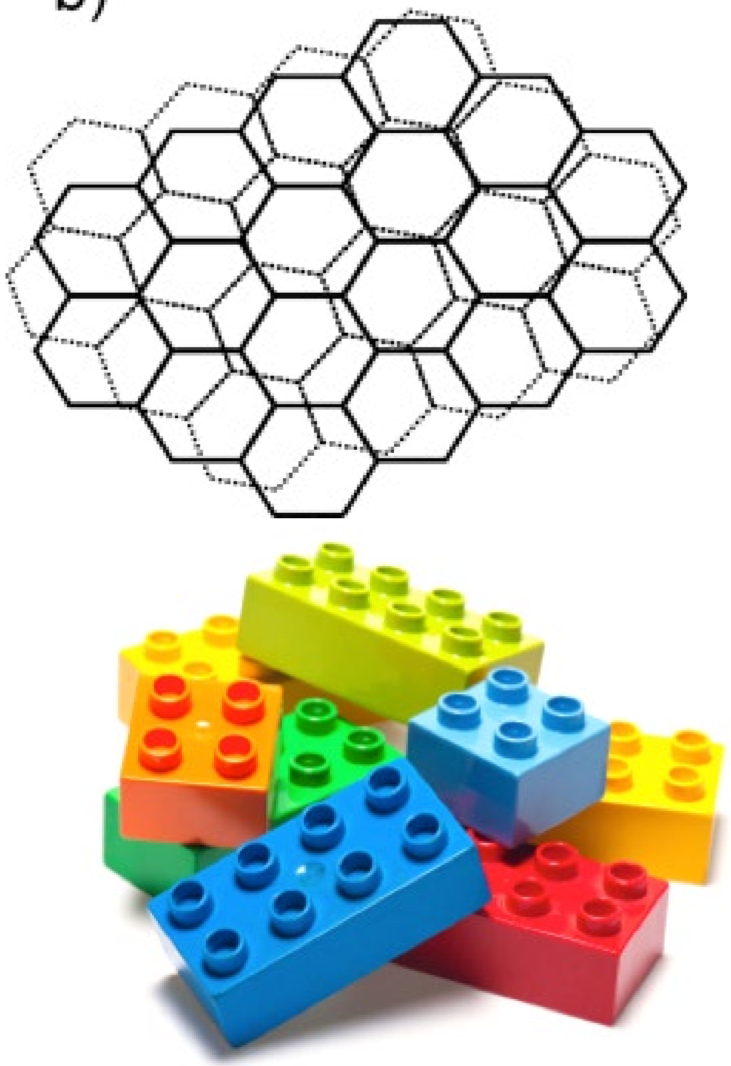
Time Temperature Dependence



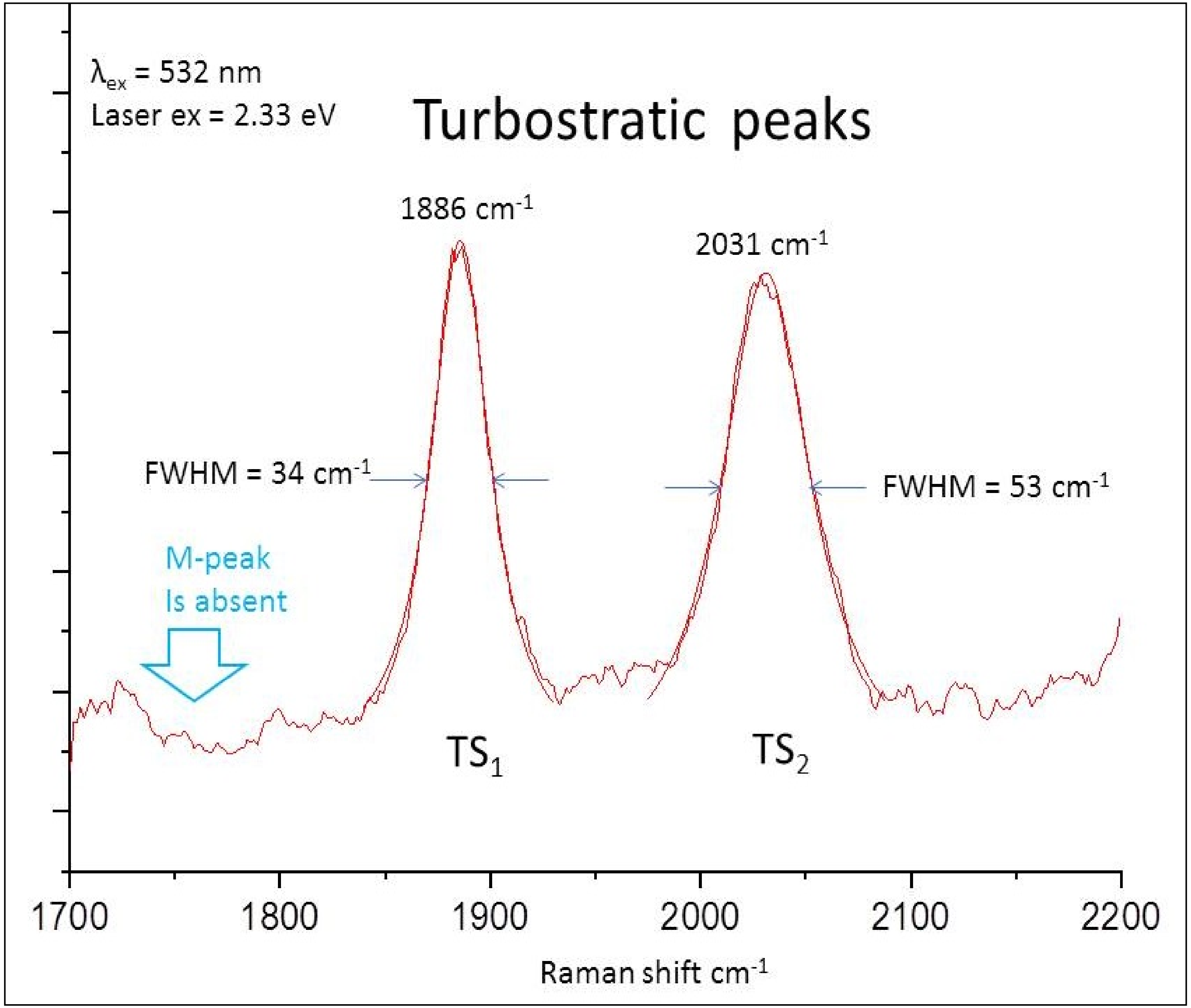
- Temperature needs to reach 3000 K for graphene conversion
- Pulse duration less than 50 ms for best graphene quality
- Cooling rate does not contribute to the quality of graphene

a) AB-stacked (Bernal) vs. b) turbostratic graphene



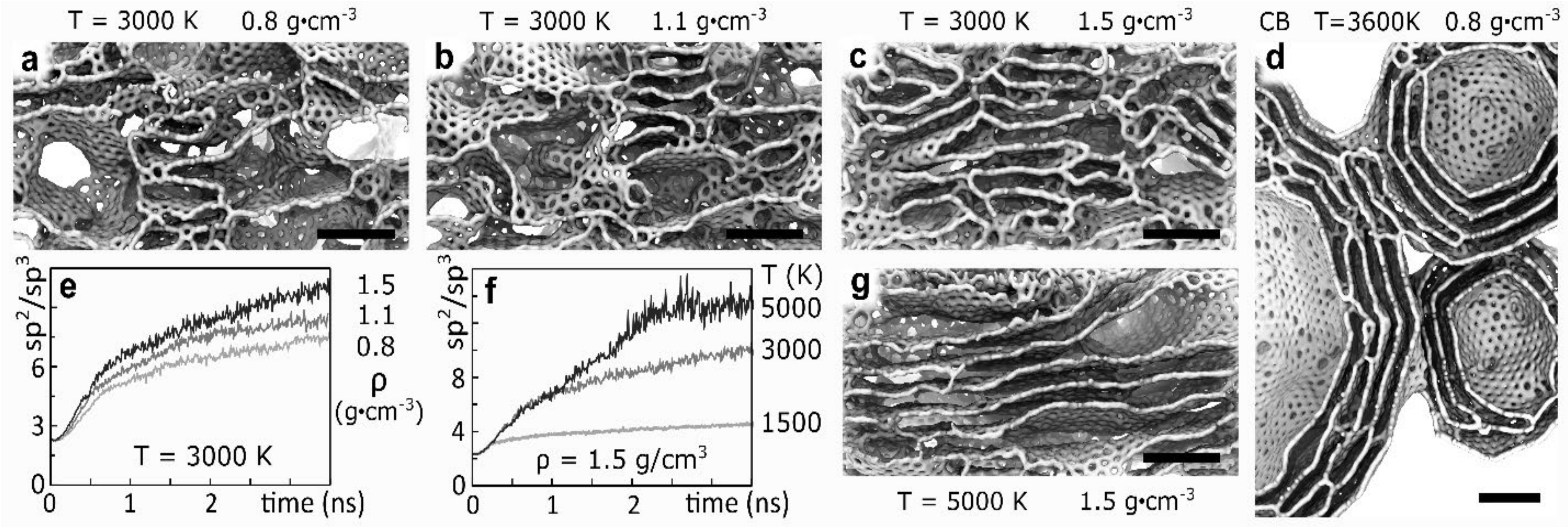


https://doi.org/10.1002/smll.200901173



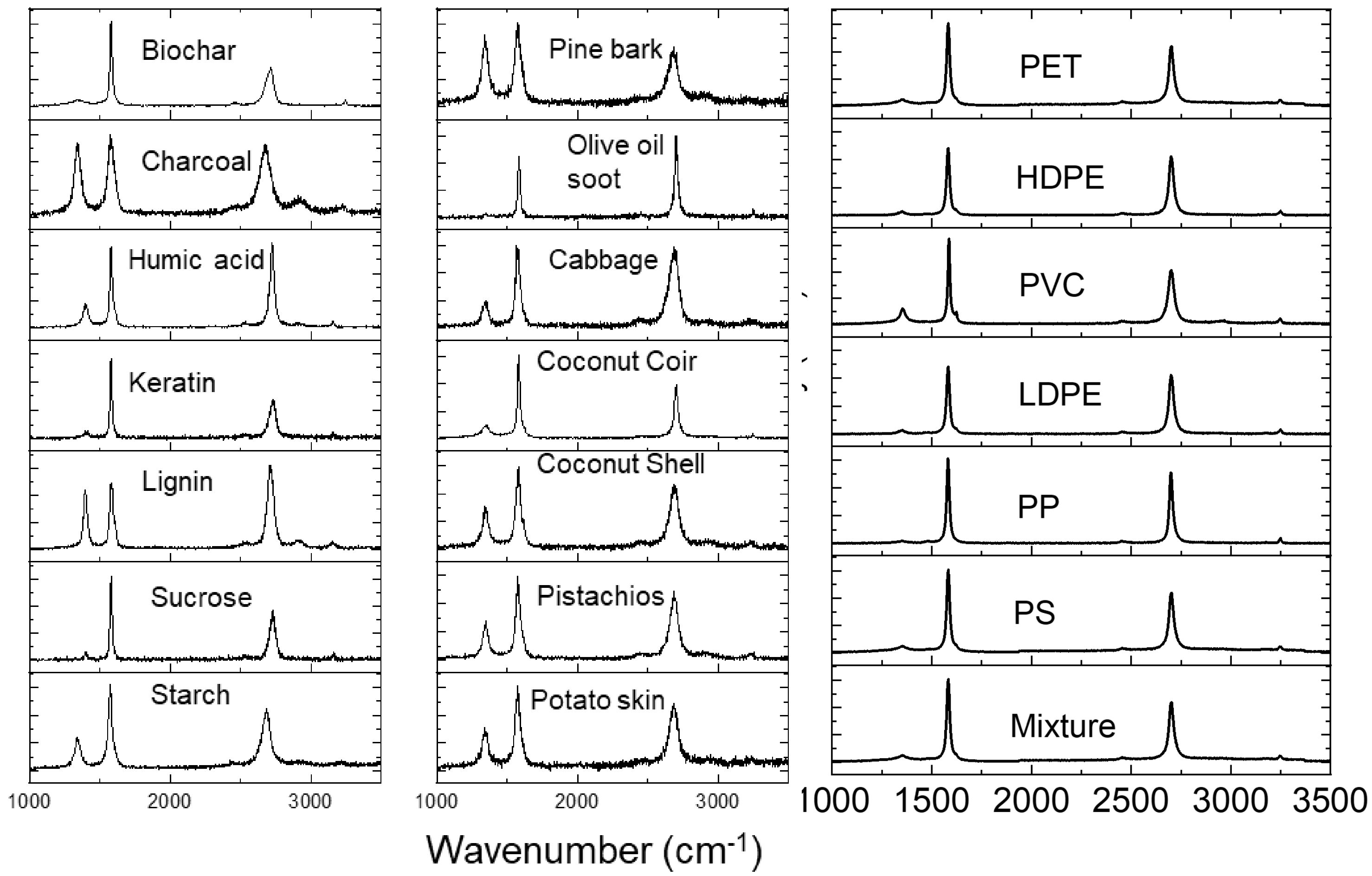
Turbostratic peaks in the Raman spectrum of CB-FG. $I_{G/TS1}$ ~30. Lorentzian fit is shown as a superimposed smooth line. The R-squared is 0.994 for TS_1 and 0.99 for TS_2. These excellent fits indicate the high quality of the FG and the unmistakable presence of these Raman lines are attributable to turbostratic graphene.

Simulations



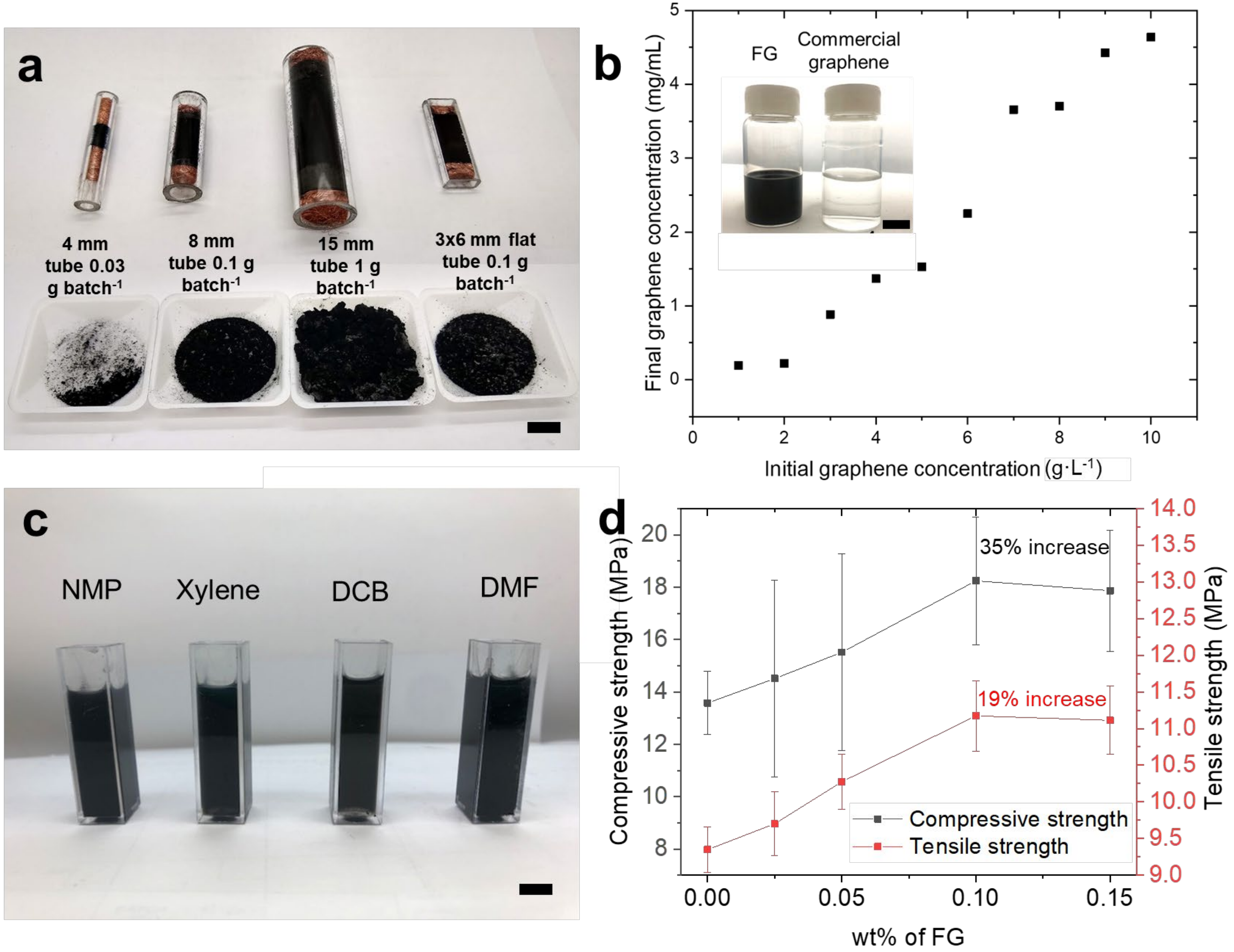
Molecular dynamics (MD) simulations of structures with various characteristics (such as micro-porosity, misalignment, and size of graphitic domains) kept at a given temperature range (1500 to 5000 K) for a prolonged time (up to 5×10^{-9} s, with NVT thermostat). Sample structure after annealing at 3000 K for carbon materials of various densities: **a**, 0.8 g·cm^{-3}, sponge-like structure; **b**, 1.1 g·cm^{-3}; **c**, 1.5 g·cm^{-3}, high degree of graphitization. **d**, Carbon black with 0.8 g.cm^{-3} density and large macro-porosity after prolonged (5×10^{-9} s) annealing at 3600 K, polygonal fringes are apparent. **e-f**, Change of structural composition of materials during annealing with different densities and temperatures. **g**. 1.5 g·cm^{-3} structure after annealing at 5000 K, initial structure is the same as for c. Scale bars are 1.5 nm.

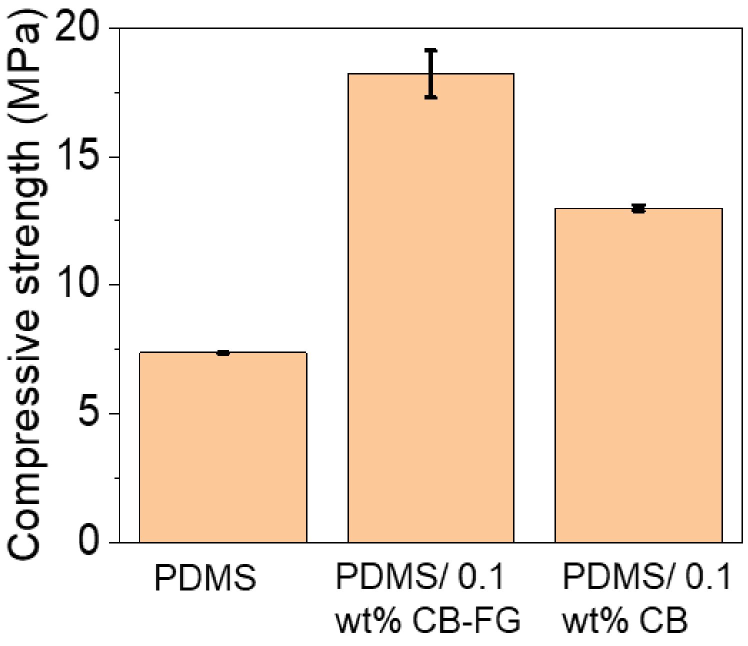
Flash graphene from “any” solid carbon source



Carbon black, anthracite coal, calcined coke, used coffee grounds, charcoal, biochar, humic acid, keratin (human hair), lignin, sucrose, starch, pine bark, olive oil soot, cabbage, coconut, pistachio shells, potato skins, rubber tires, polymers including: polyethylene terephthalate (PET or PETE), high- or low-density polyethylene (HDPE, LDPE), polyvinyl chloride (PVC), polypropylene (PP), polyacrylonitrile (PAN), or mixed plastics.

Laboratory Scale-up FJH V2.1



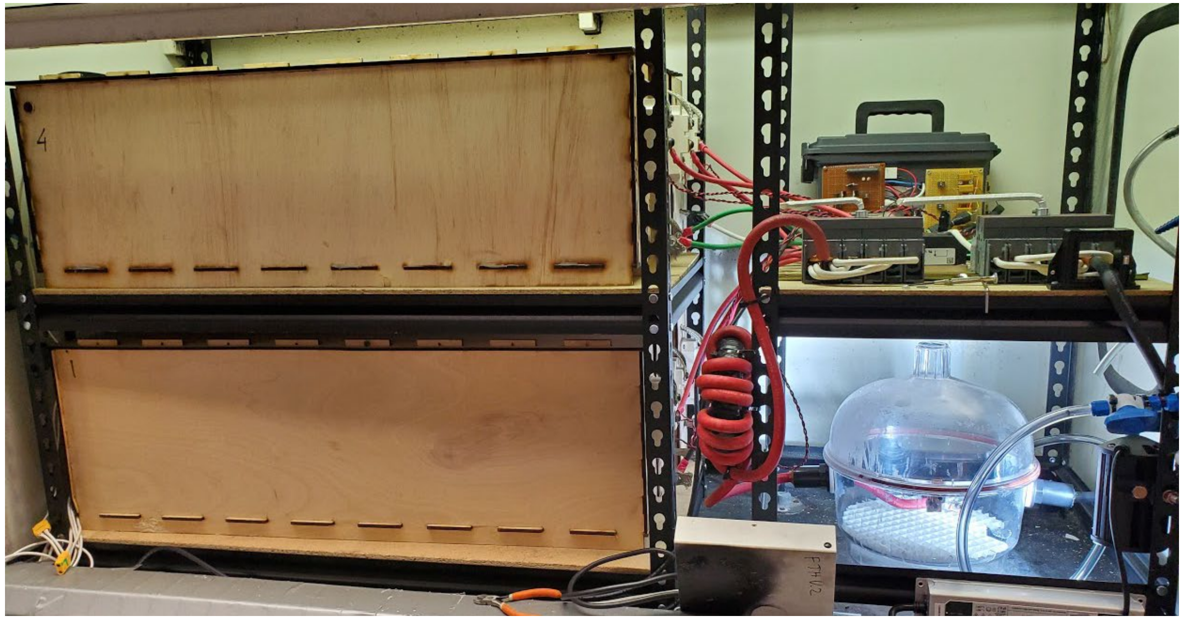


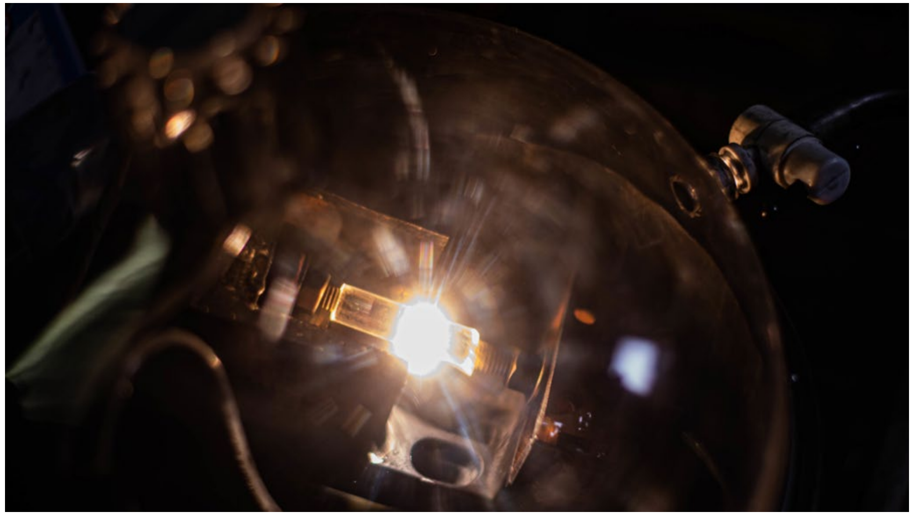
DOE-funded scale-up

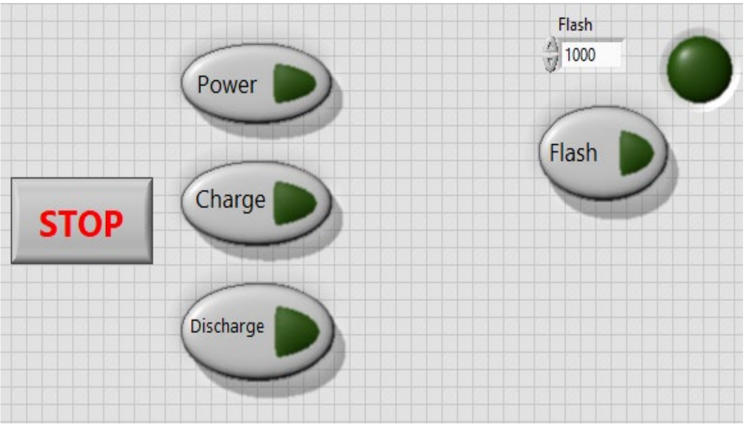
Convert a US Coal Product Into 1 kg of Graphene Per Day

Can this really be a viably scaled method?

FJH 5.0

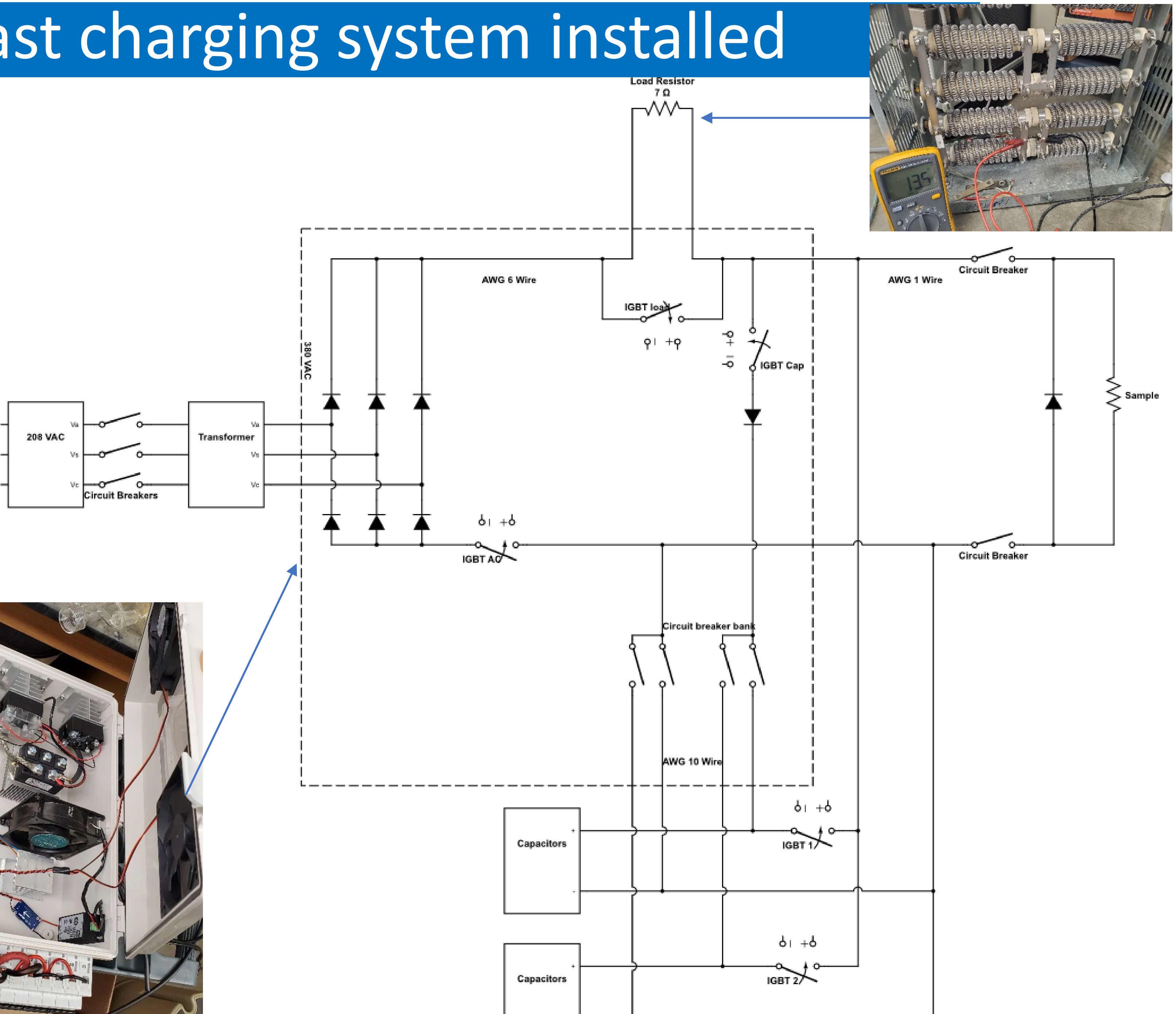




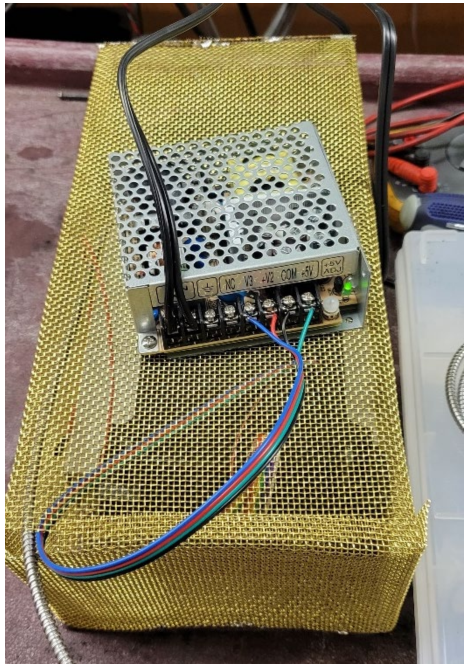


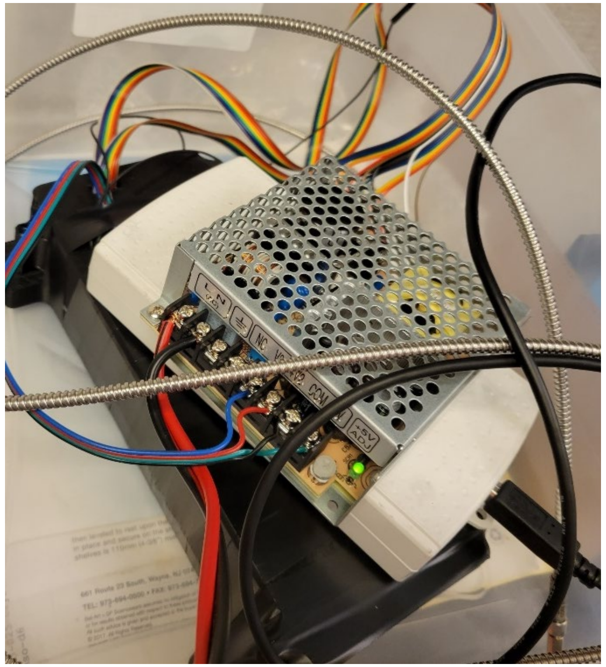
New fast charging system installed

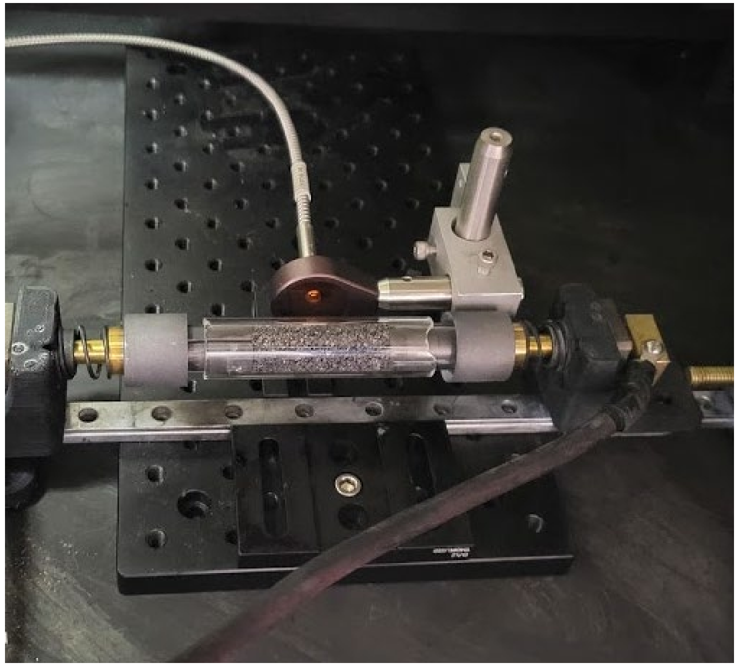
- 19 s charging system, 8X faster than previous version at 70% power capability.
- Theoretically, we can get up to 0.96 kg/h.



New spectrometer

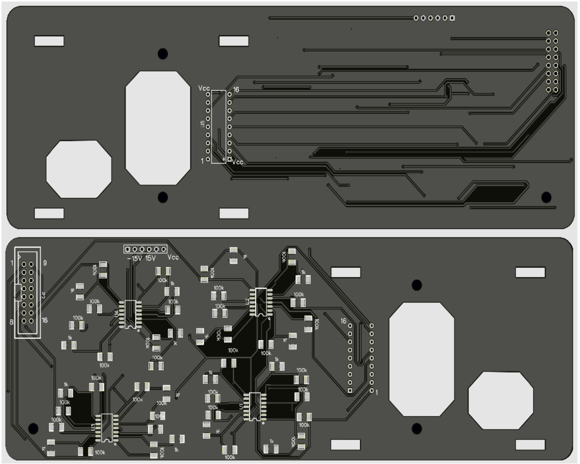


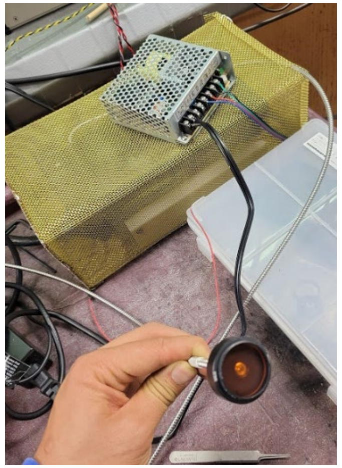




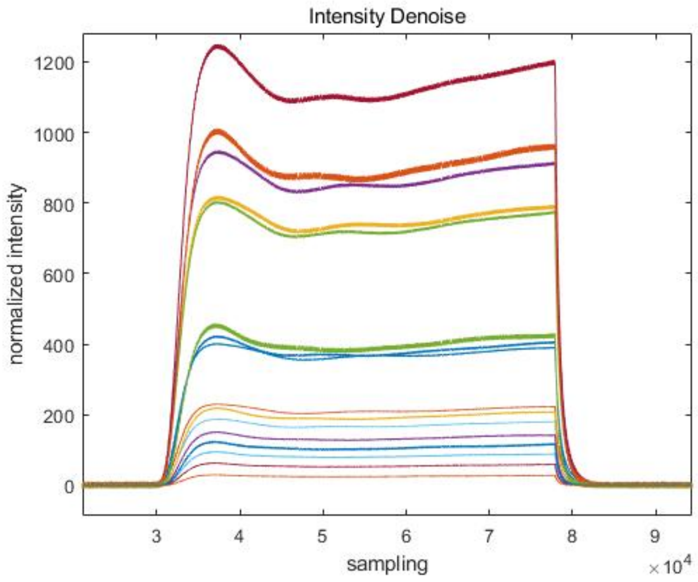
- Successfully build and deploy two spectrometers to two of our FJH system.
- Both work well to collect the temperature profile.
- Filter was used to protect the optical fiber end from exploding sample.

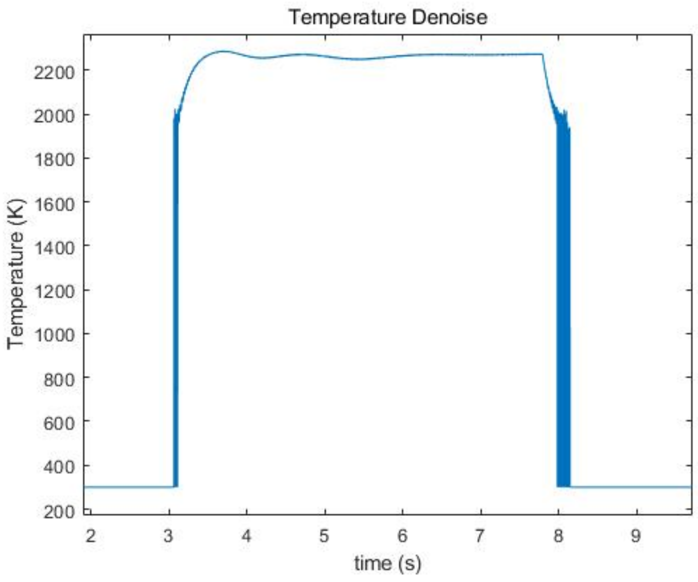
Customized Spectrometer



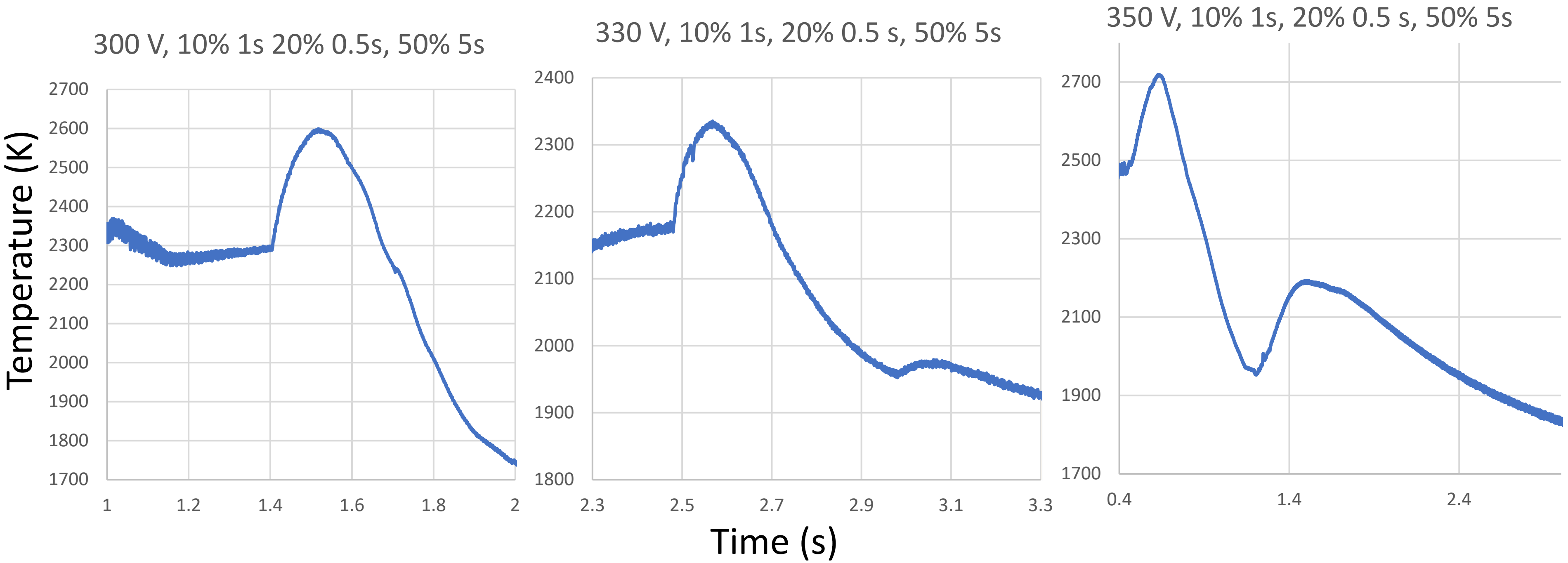


- Single board PCB design with photodiode and amplification system
- System is placed inside a Faraday cage
- Good data acquisition



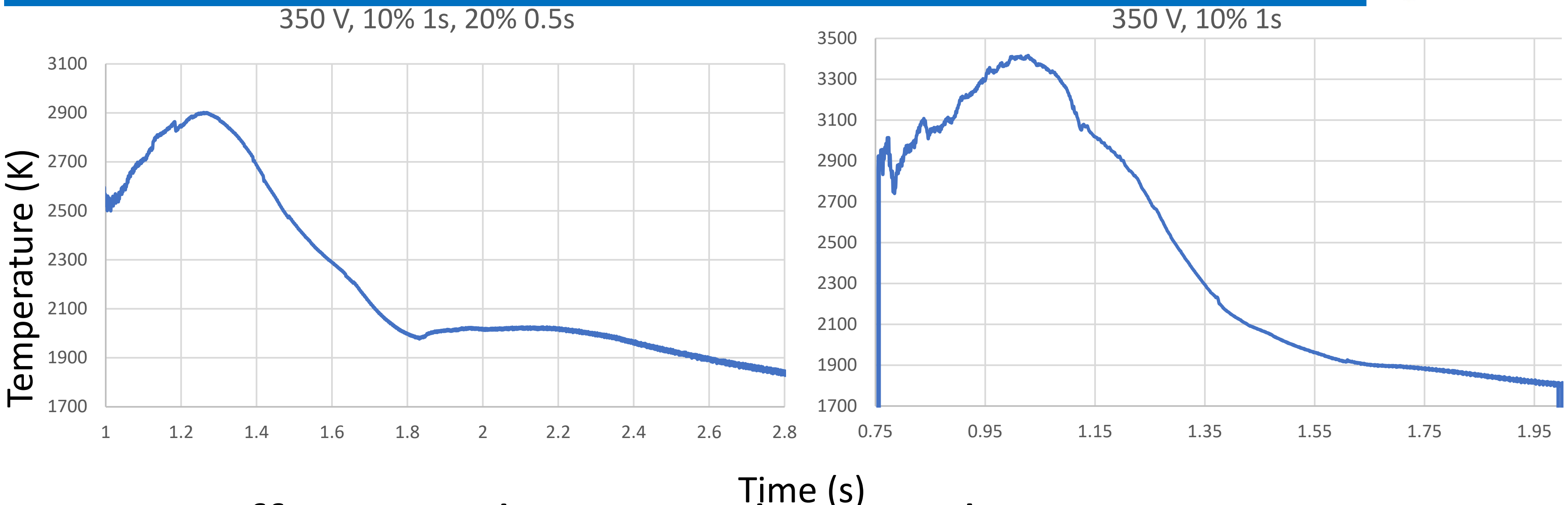


Spectrometer results



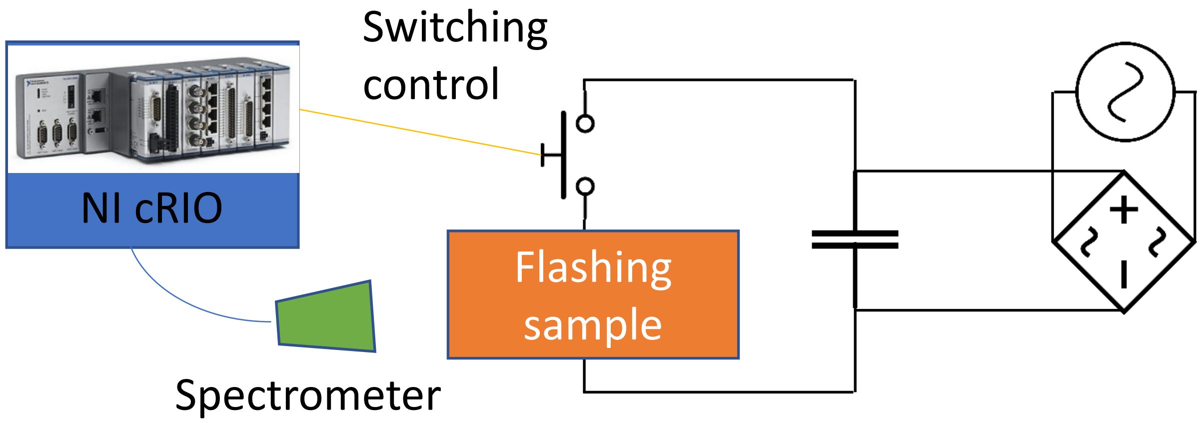
- 5 g Metcoke at same VFD sequence but different voltage sample.
- All sample reach similar peak temperature within the first sequence at 10% duty cycle.
- 20% and 50% is found only to prolong the heat and might not even necessary.

Spectrometer results



- Cut off 20% and 50% result in similar maximum flashing temperature.
- However, the graphene quality decrease base on Raman. But dispersion show similar or even better for this graphene due to more turbostratic structure.
- Energy requirement reduce from 7.5 to 5.2 kJ/g. Charging time might decrease 30% as well.

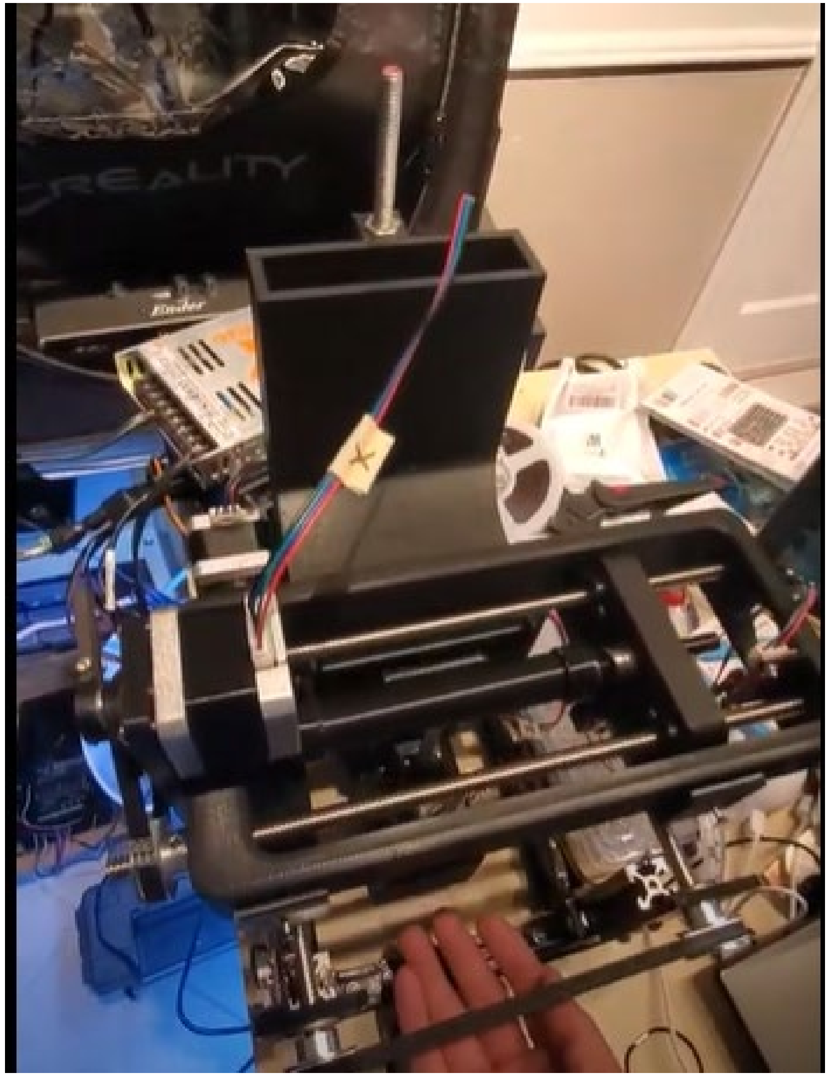
Temperature feedback system



- Control the flashing temperature with PID
- Spectrometer or IR thermometer as feedback

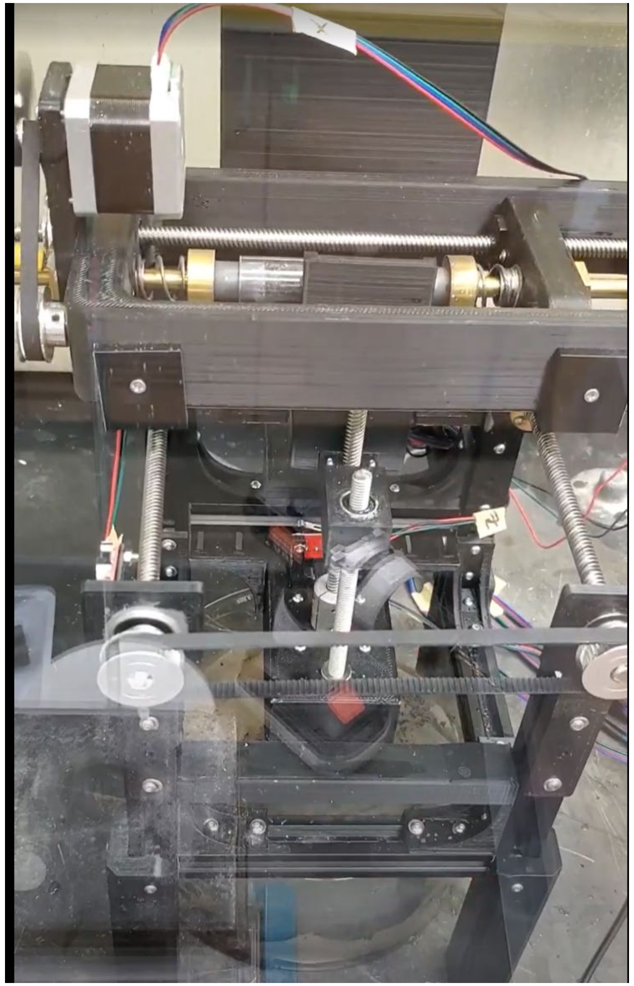
Powder flashing automation

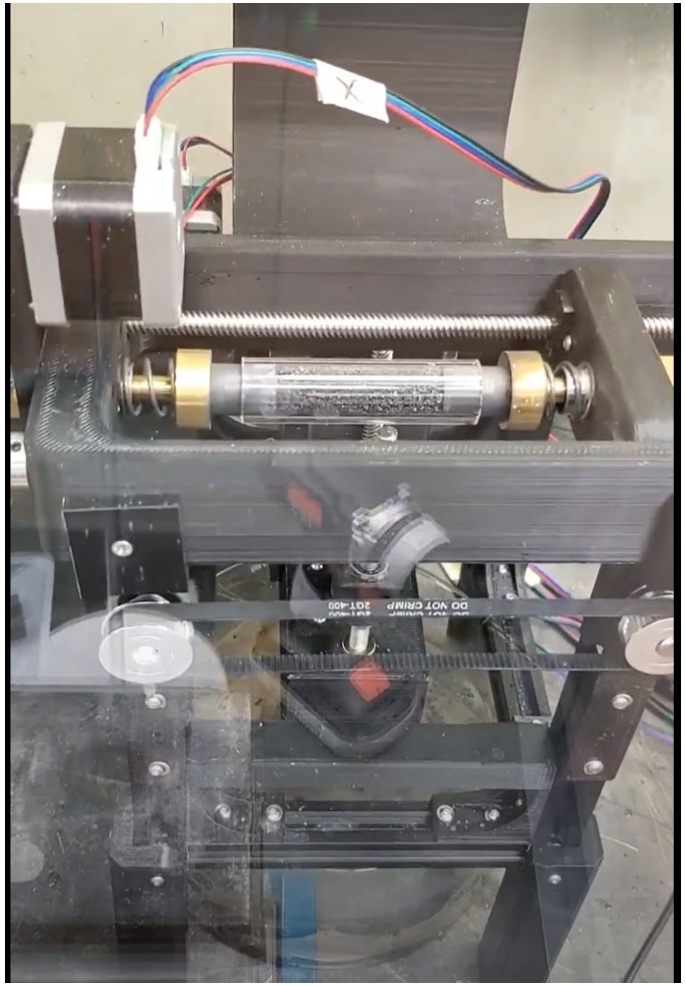
- Building automation using 3D printed parts
- Aiming for 1 batch/min (5 g/min, 7.2 kg/24 h).
- 5.7 g of coal per batch to provide > 5.0 g flash graphene per batch
- Voltage: 350-400 V
- Process yield: > 90%, graphene yield: ~100%.



Flash Joule Heating automation

- Automation of Flash Joule Heating graphene is fabricated from 3D printed parts. >90% processing yield with ~100% excellent quality graphene.





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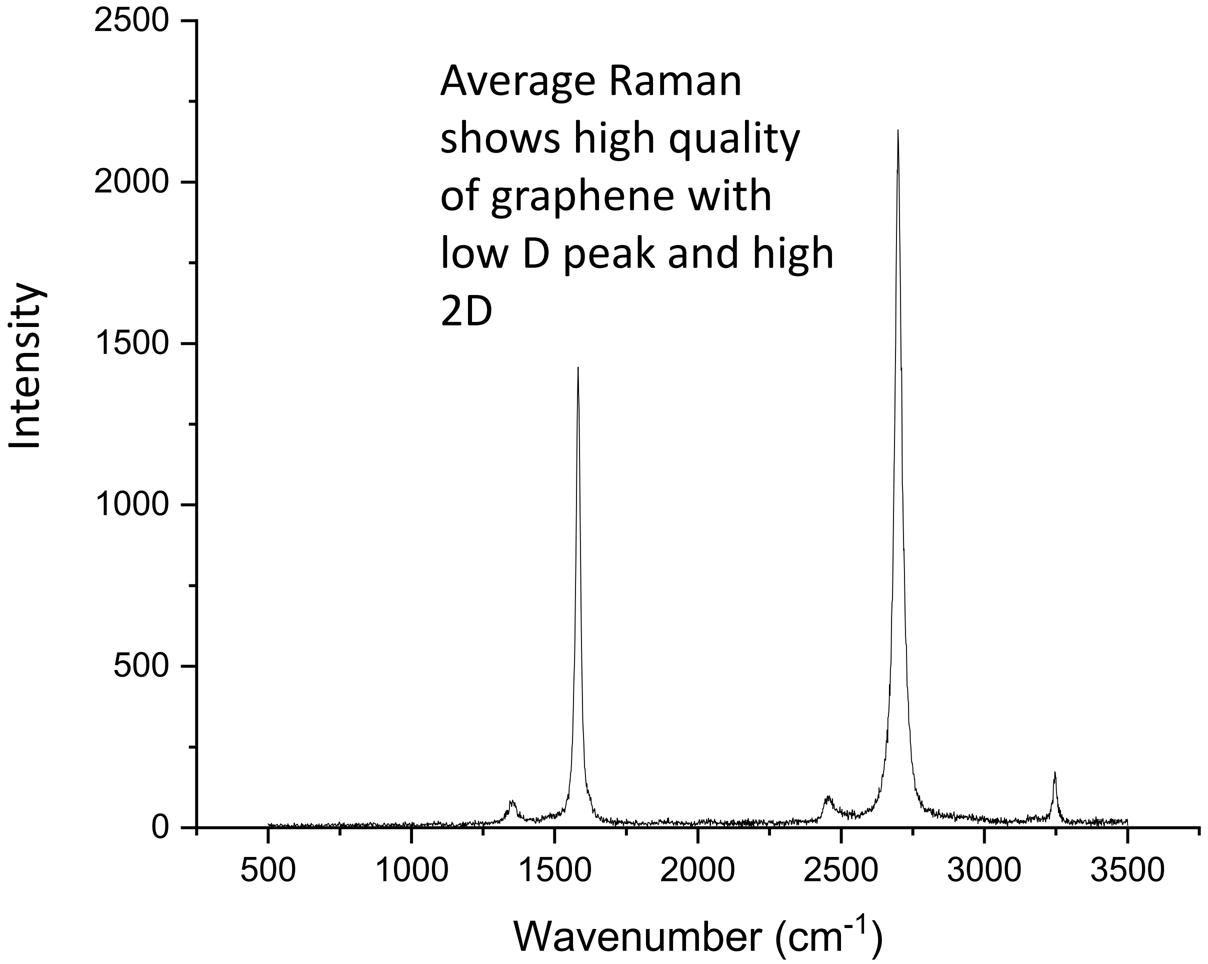
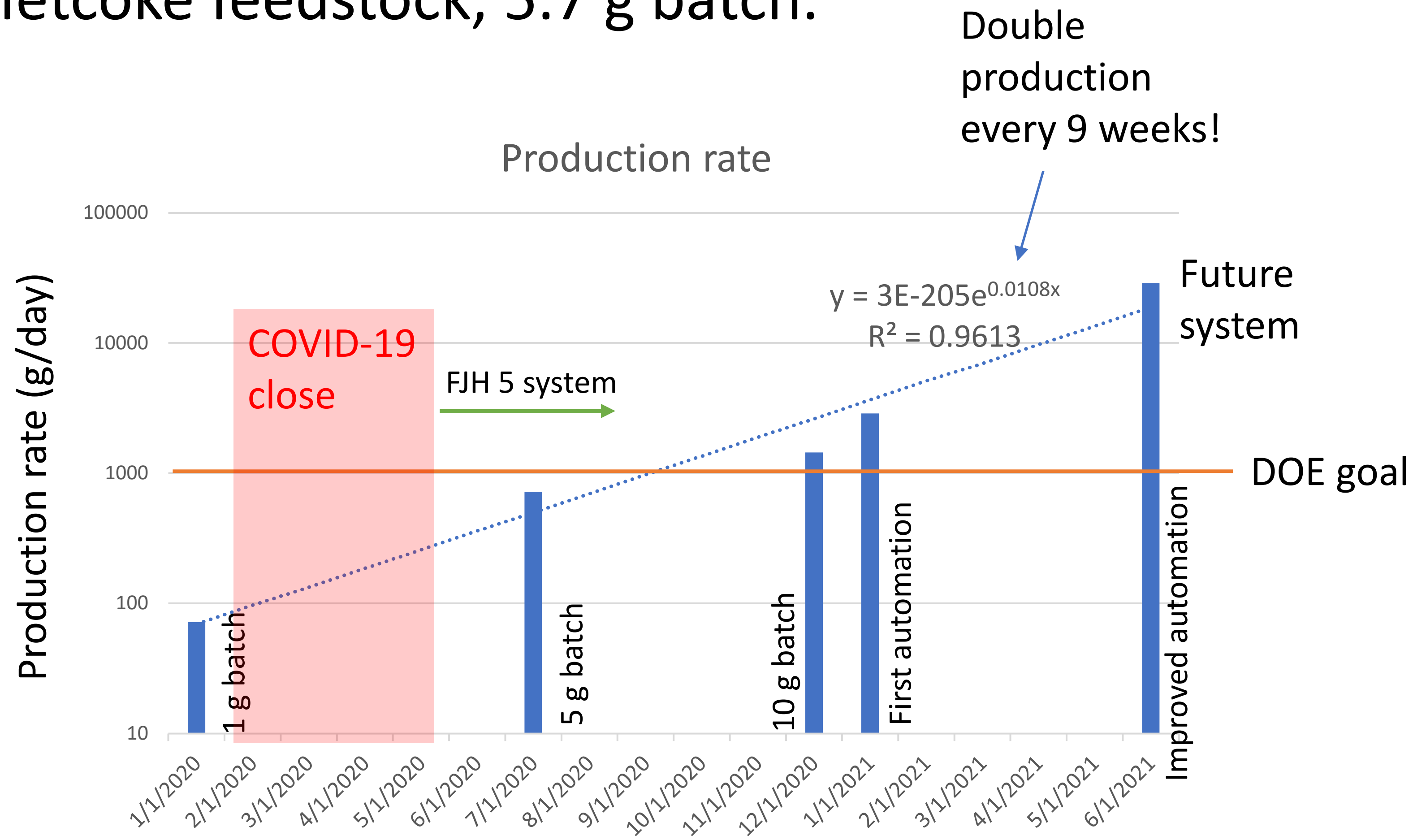


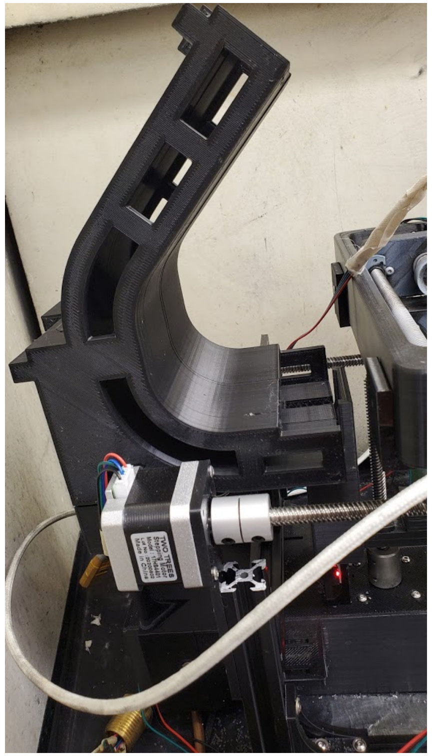
Previous automation work

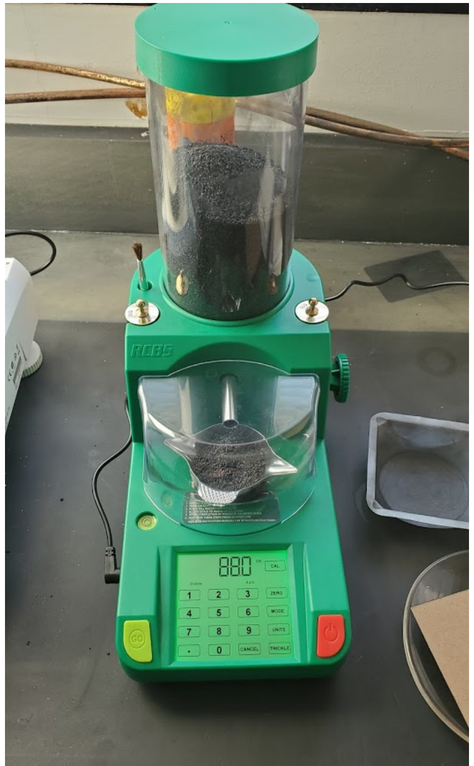
- Complete the automation with 2 g/min production rate.
- Metcoke feedstock, 5.7 g batch.



1 kg milestone preparation

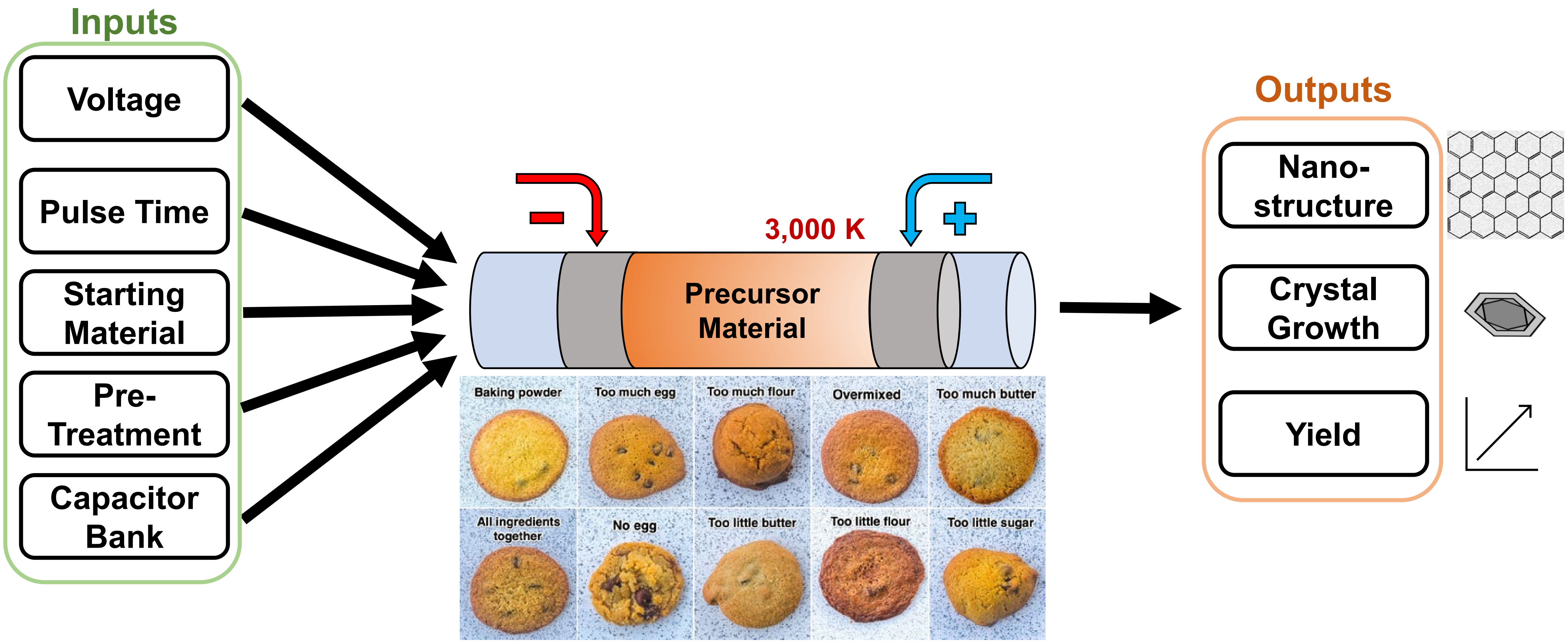
- 200 quartz tubes
- 60 graphite electrodes
- 1.2 kg of metcoke ground to 0.6-1.2 mm size
- Automation scale
- Graphite cleaning tumbler (bullet shell cleaner only $60 on Amazon)
- Metcoke (coal) weighing station (bullet gunpowder dispenser only $300 Amazon)
- Replaceable magazines and brass electrodes





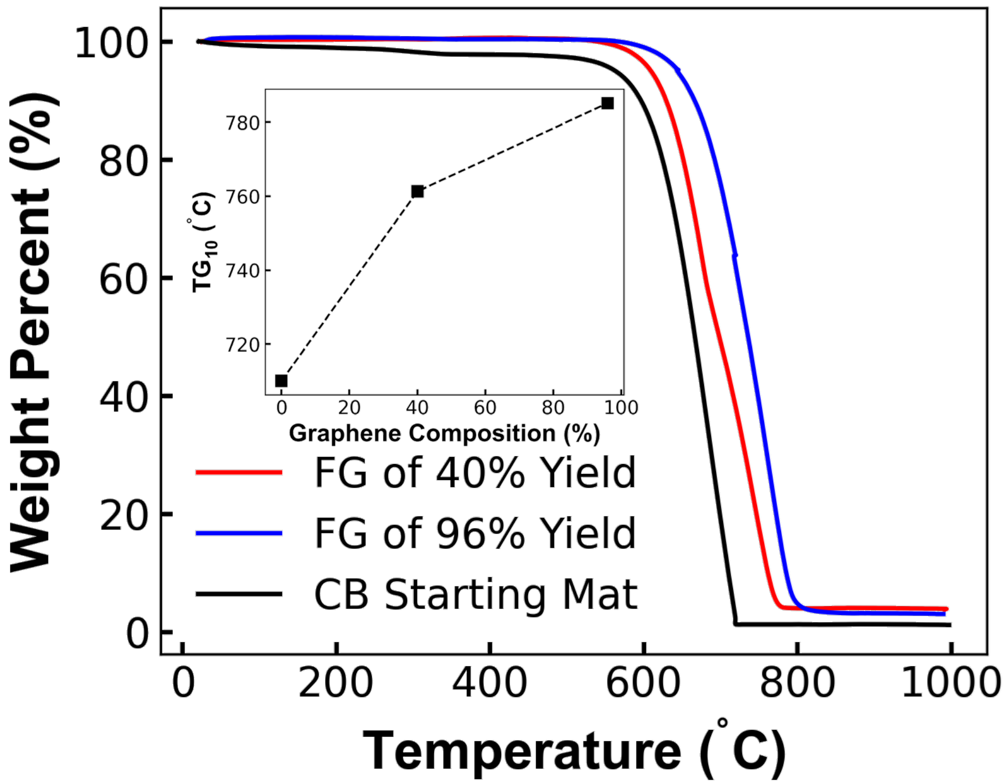
Roll over image to zoom in

Understanding nanomaterial formation by FJH requires study of a large parameter space

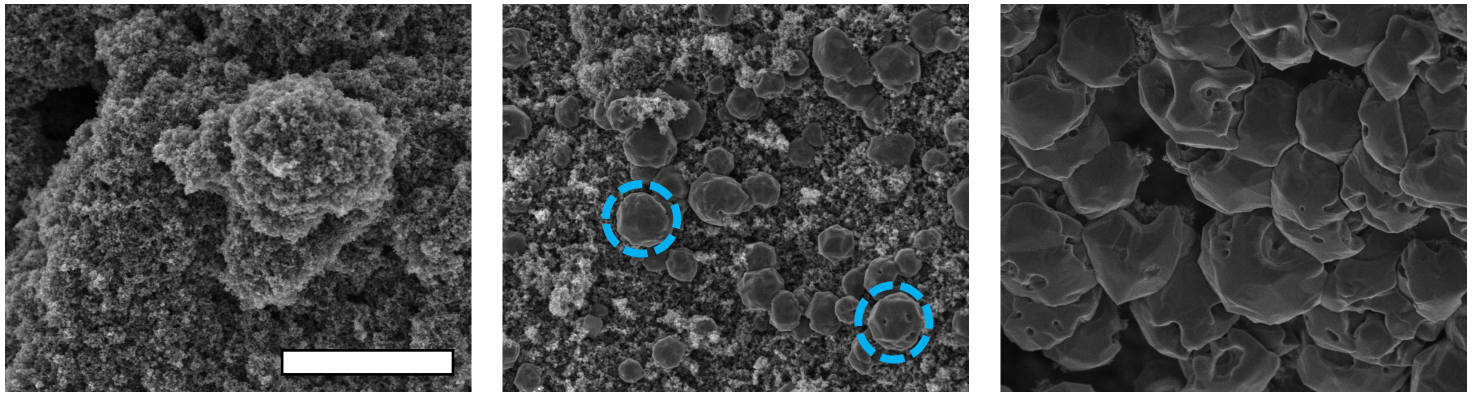


Zhang, J. et al. *Mat. Today,* **2020**, *40*, 132.

The "graphene yield" metric possesses validity as an indicator of bulk crystallinity



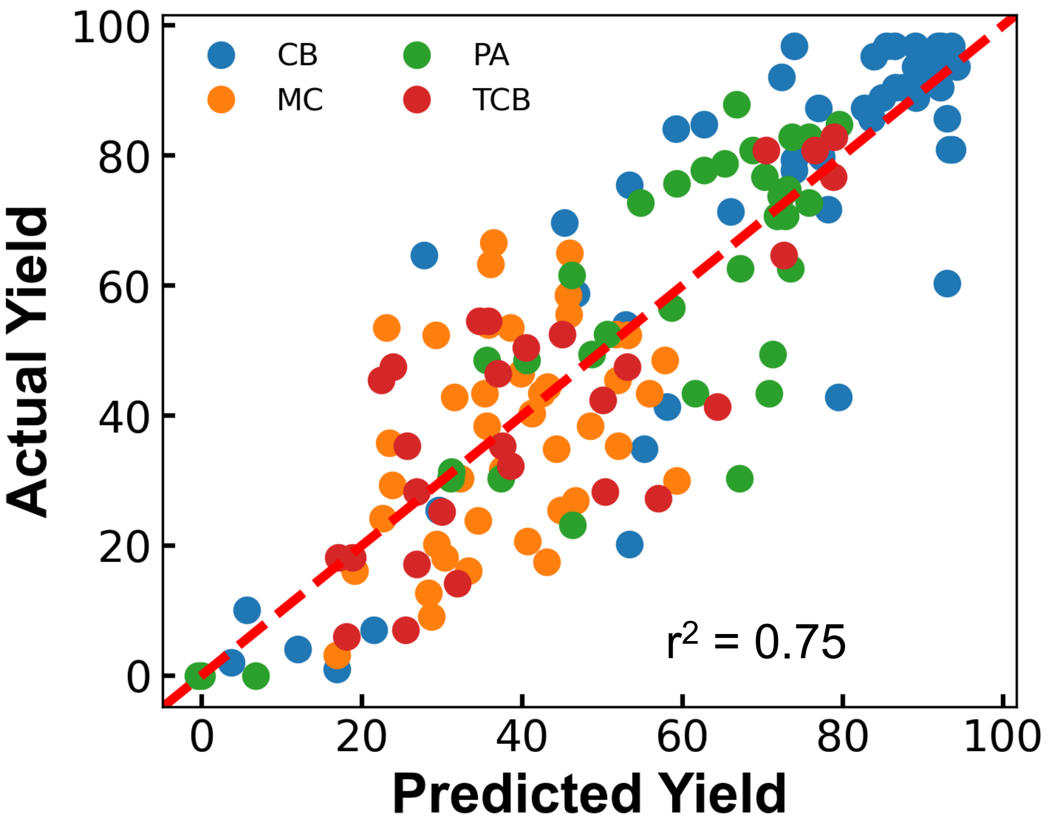
Graphene yield provides a quantitative measure of sample crystallinity and is predictive of thermal stability and other properties. Hence, GY is the most accurate way we've devised to assess bulk properties in heterogeneous flashed materials.



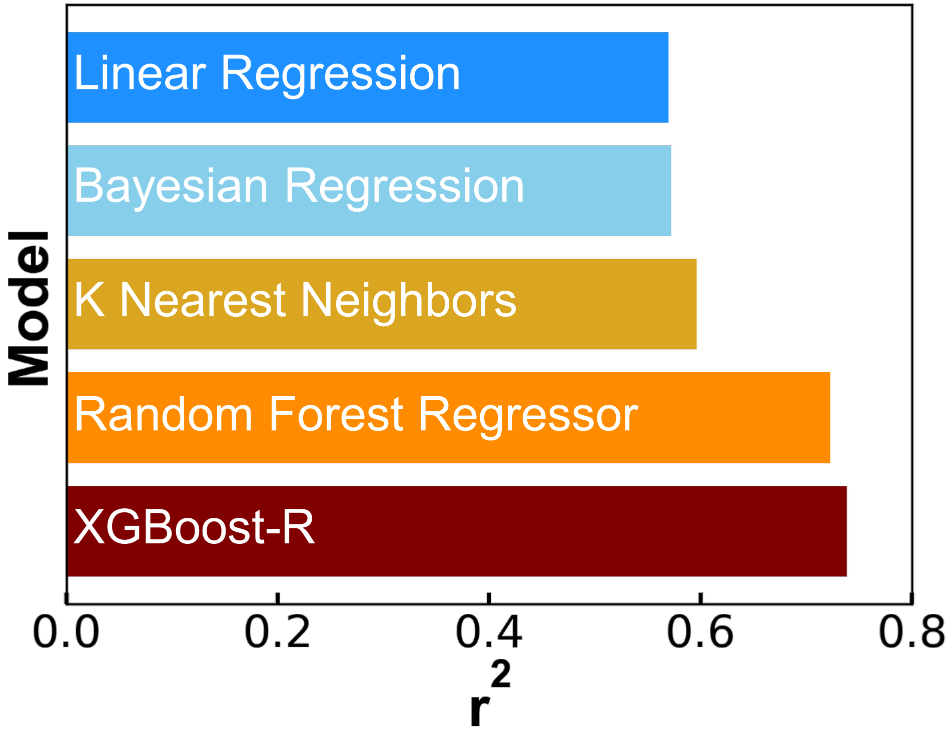
Starting Material | Intermediate Yield | High Yield

Beckham, J. L. et al. Manuscript in preparation.

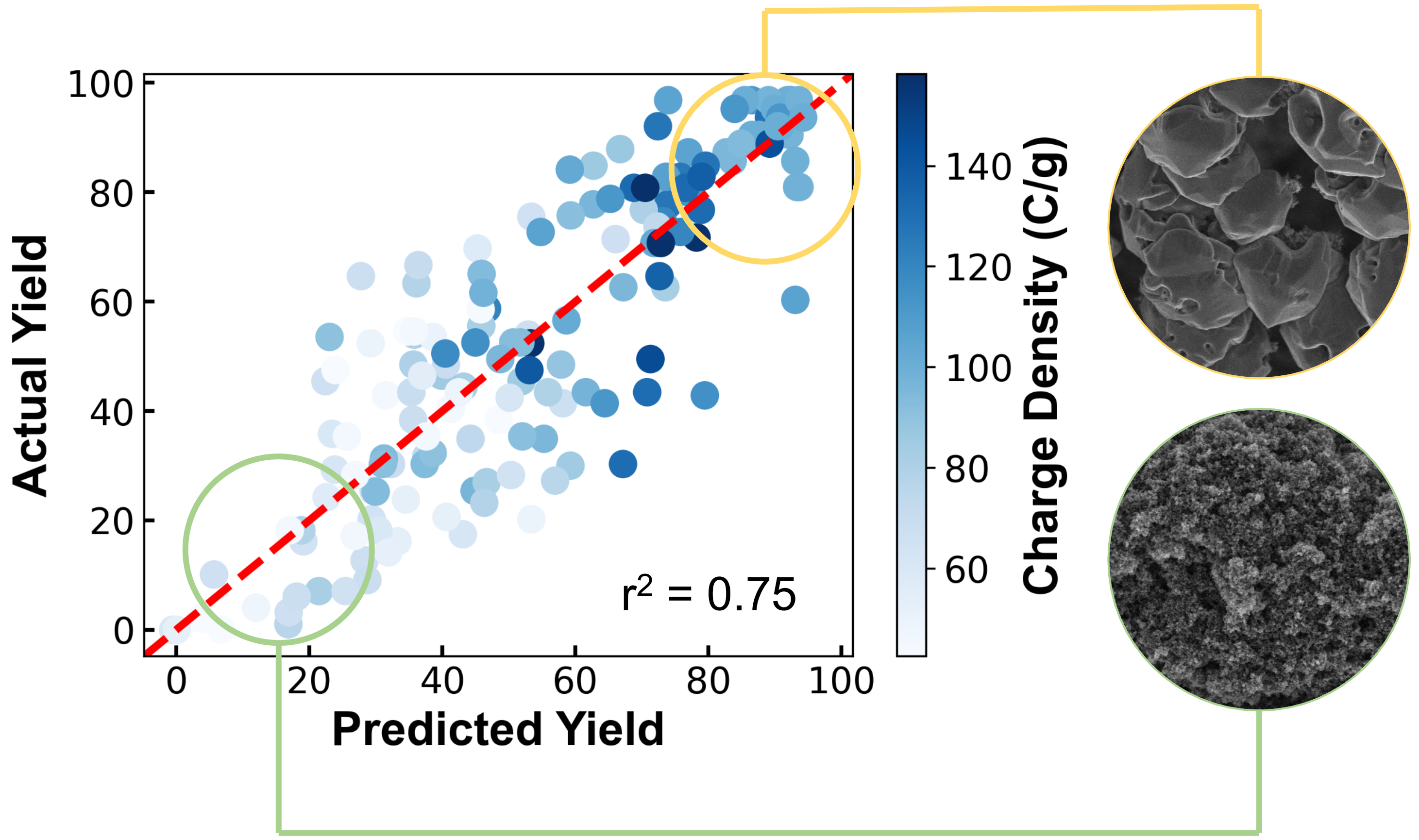
A regression model of graphene yield predicts bulk crystallinity of FG from flash parameters



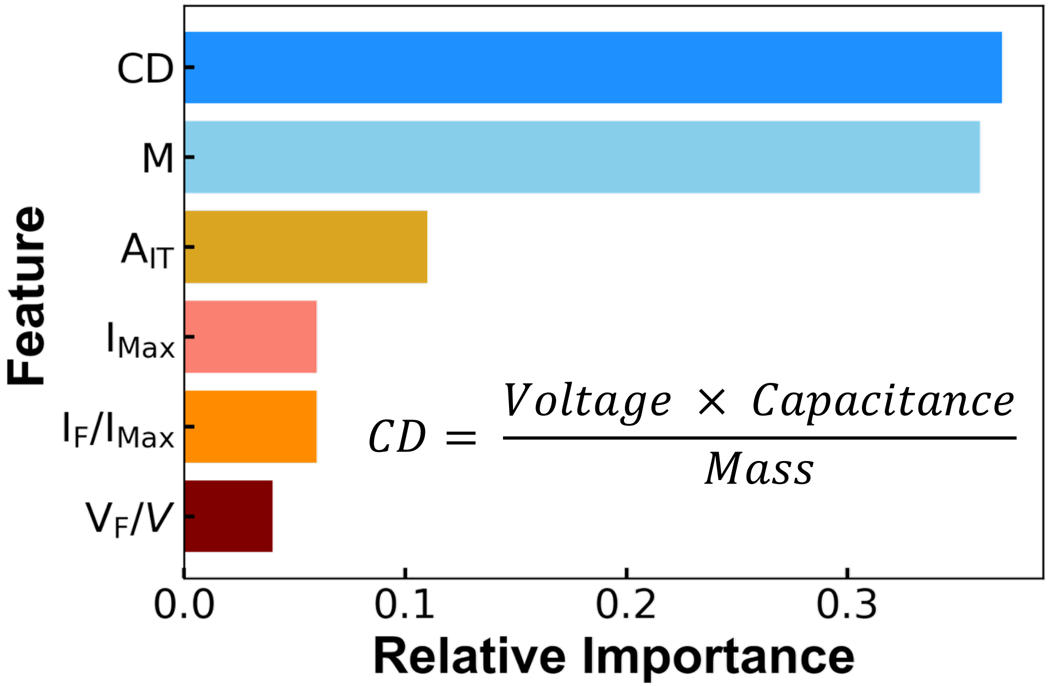
Models predict GY with MSE of ~11% (compared to baseline error of ~27%).



Feature analysis reveals the importance of charge density in predicting graphene yield

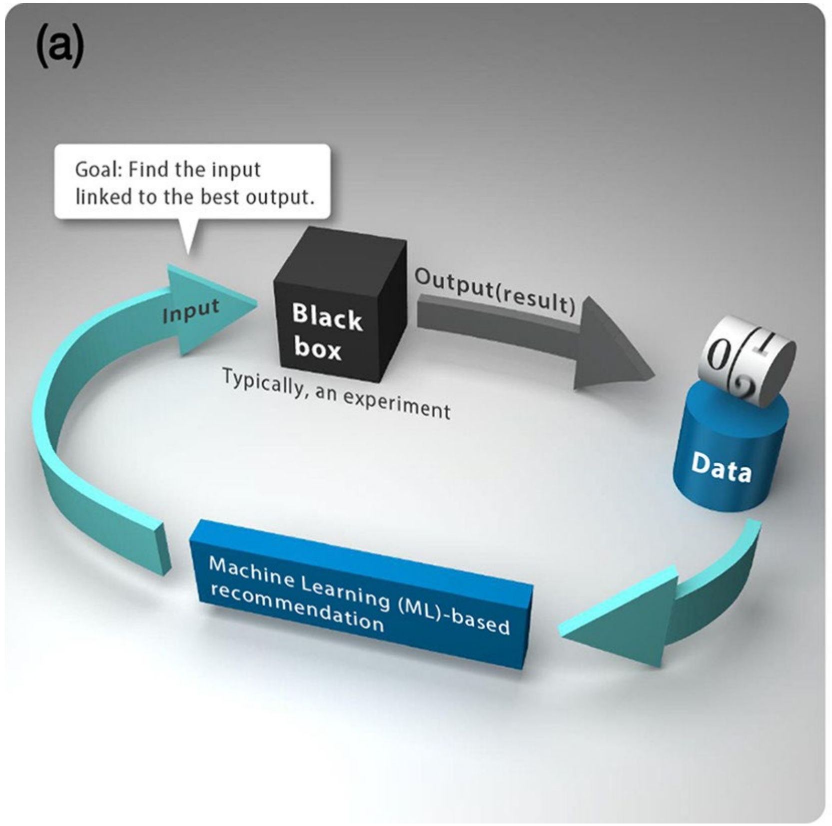


Six features were chosen empirically amongst ~30 tested options.

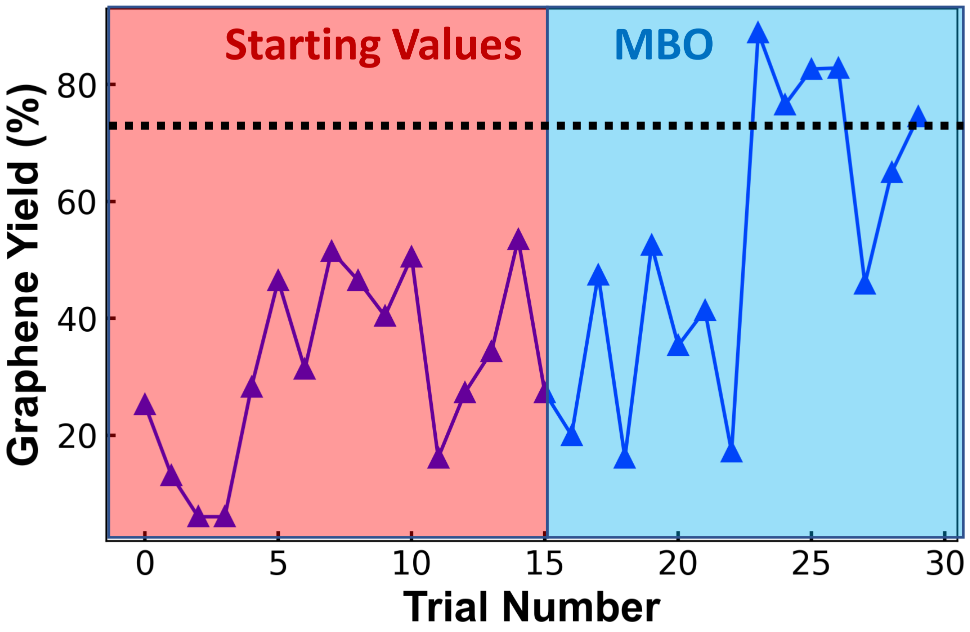


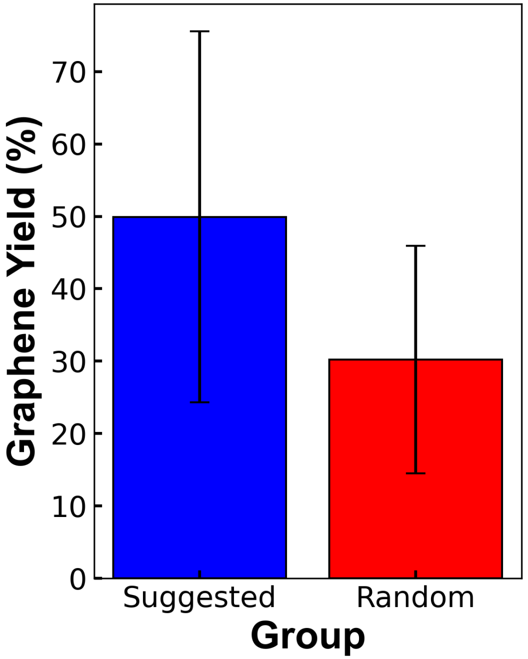
Beckham, J. L. et al. Manuscript in preparation.

Model-Based Optimization for Autonomous Synthesis



Model-based Bayesian optimization implemented in R allowed the improvement of graphene yield from a negative-value feedstock in only 8 trials.

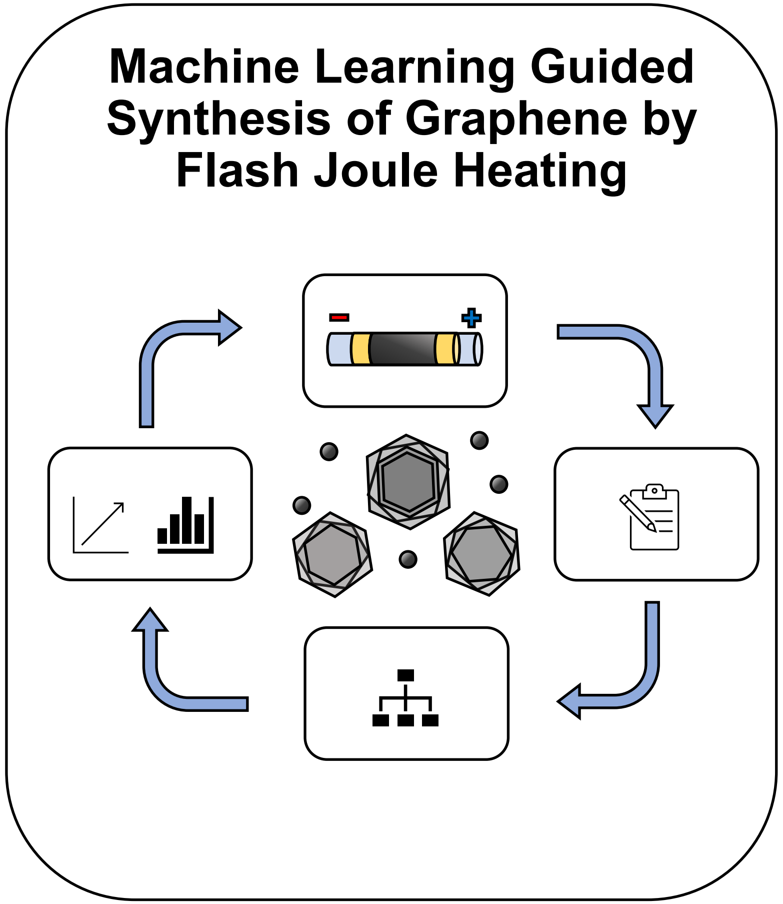




Salley, D. et al. *Nature Comm.*, **2020.**

Machine Learning Summary

- Achieved prediction of graphene yield that improves significantly compared to baseline predictions.
- Developed methodology for assessing bulk crystal formation during FJH.
- Used the constructed model to test hypotheses regarding the FJH process that improved our understanding.
  - Dependence on energy density
  - Importance of “black box” parameters
  - Effect of starting material



Milestone Format

Working on now

Task/ Subtask	Milestone Title & Description	Planned Completion Date	Revised Completion Date	Actual Completion Date	Verification method
1.0	**Project management plan**	31 Oct 2019			
2.0	**In depth study of FJH graphene process**	1 Dec 2020			
2.1*	In-depth study of FG materials properties	25 Feb 2020			
2.2	Simulation of electrical input into molecular dynamics calculations for FG formation	24 April 2020			
2.3	Machine learning program V1.0 for flash optimization—verification of usefulness	1 Dec 2020			
2.4	Estimation of grinding	7 May 2020			
3.0	**Scale up of the FJH process to 1 kg per day**	30 Sept 2021			
3.1	Reduce the conversion energy from 4 Wh/g to 2 Wh/g	15 Nov 2020		√	Report and/or publications provided.
3.2	Design of scale-up reactor for ~~10~~ 5.7 g flash	25 Feb 2020 17 July 2020		√	Report and/or publications provided.
3.3	Build V1.0 for ~~10~~ 5.7 g flash unit	25 May 2020 17 July 2020		√	Report and/or publications provided.
3.4*	~~Test V1.0 for 10 g flash unit~~ Replaced with automation	25 June 2020		√	Report and/or publications provided.
3.4	~~Optimize V1.X for 10 g flash unit Replaced with automation~~ Replaced with automation; design showed 480V required	1 Dec 2020		√	Report and/or publications provided.
3.5	~~Design of scale-up reactor for 100 g flash~~ Replaced with automation first testing	1 March 2021		√	Report and/or publications provided.
3.6*	~~Build V2.0 for 100 g flash unit~~ Replaced with automation testing for 100 g via ~20 flashes	1 June 2021		√	Report and/or publications provided.
3.7 (removed external)	~~Test V2.0 for 100 g flash unit~~	1 July 2021		√	Report and/or publications provided.
	Replaced with automation optimization for graphene quality				
3.8	~~Optimize V2.X for 100 g flash unit~~ Material preparation for final synthesis automation	1 Sept 2021			Report and/or publications provided.
3.9*	~~11x 100g flash to afford 1 kg FG in a 24 h period~~ Automated repeated 5.7 g flashing to produce 1 kg FG in 24 h	30 Sept 2021			Report and/or publications provided.

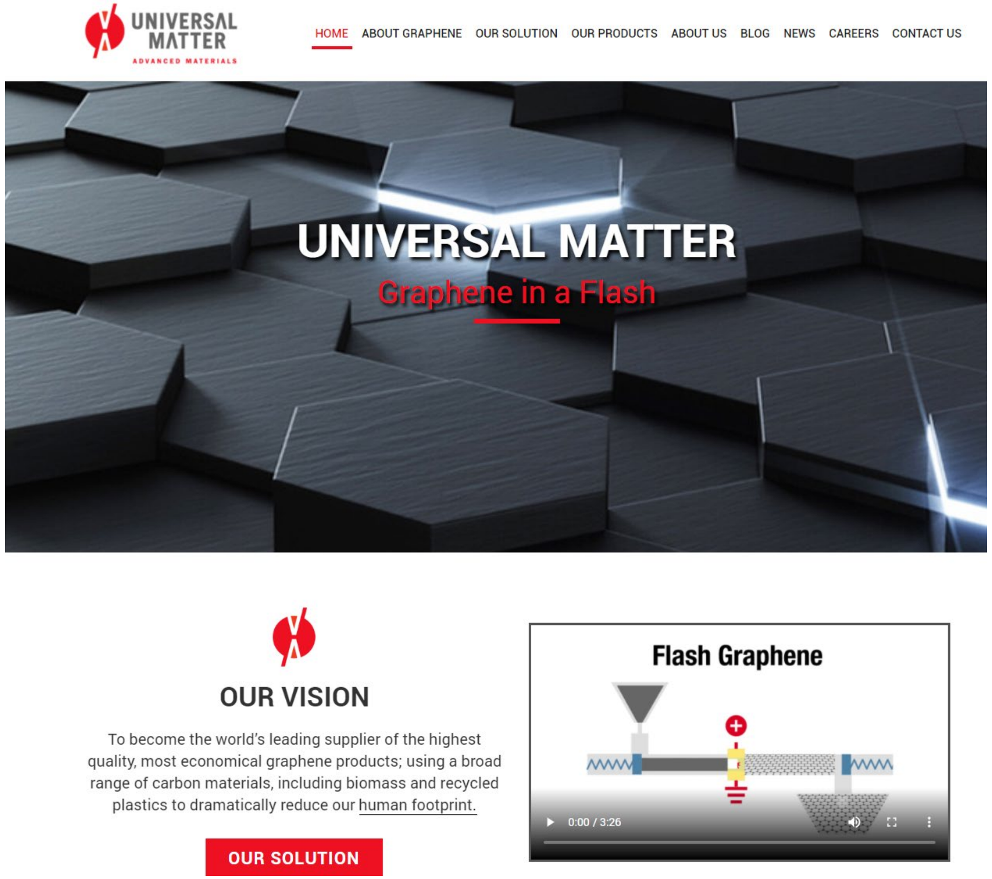
*External Milestone

Start-up Company

www.universalmatter.com

1 ton per day in 14 months

100 tons per day in 28 months



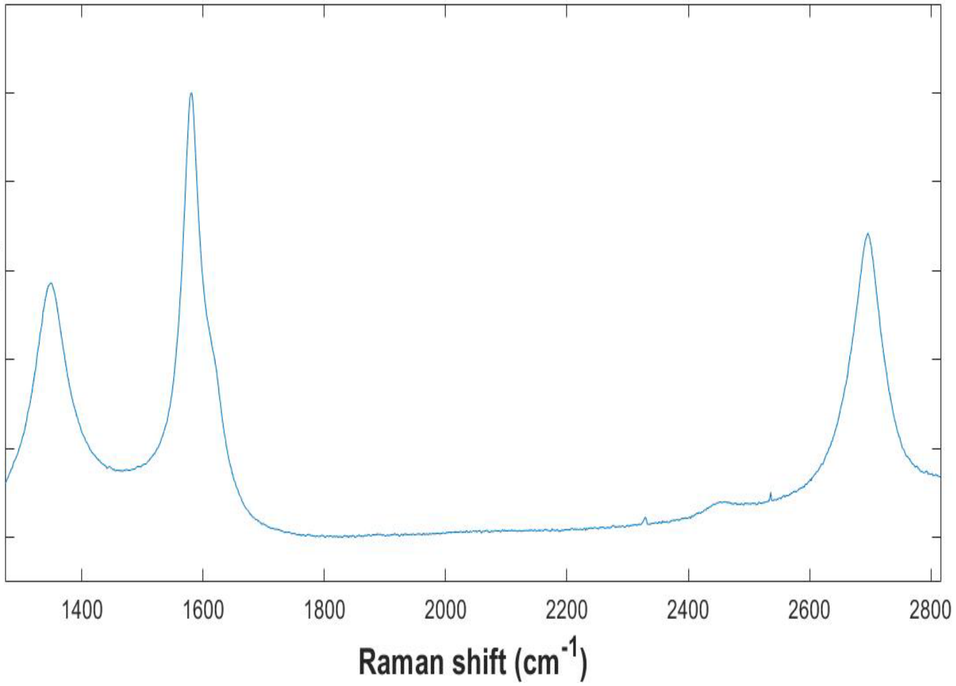
Tangential Benefits Discovered

- Mixed waste plastic to graphene at $35 per ton
- Waste fuel oil to graphene for diesel stabilization
- Lowering the coefficient of friction for mechanical oils– with Argonne National Lab

End-of-Live Vehicle Waste Plastic (ELV-WP)

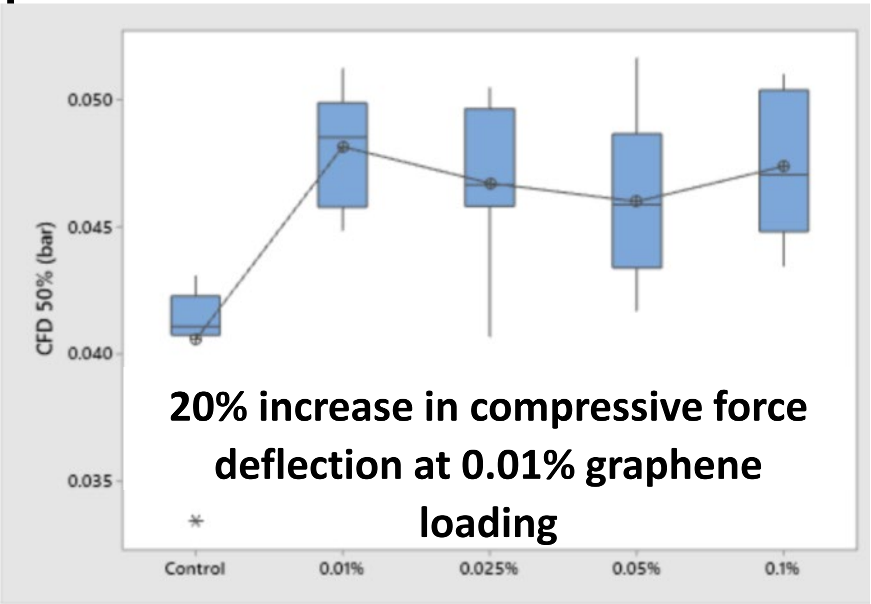
- Plastic in vehicles is only increasing (~175 kg), with more stringent disposal guidelines being implemented
- Ford Motor company sent us some from a landfill (dirty!)
- Through simple hammermill grinding with 5% metcoke and ACDC, we synthesized high quality graphene

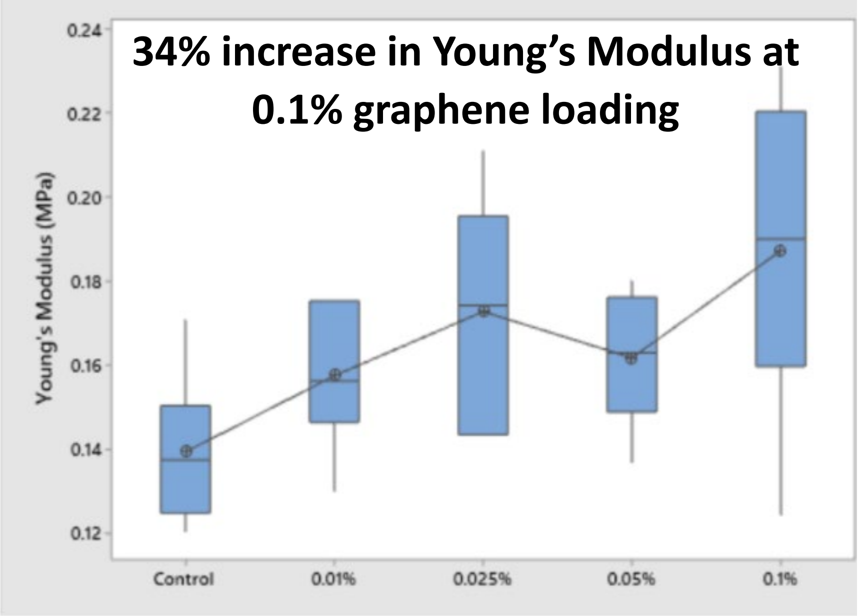
Average Spectra of 100 Spots from 15 g of ELV-WP Graphene



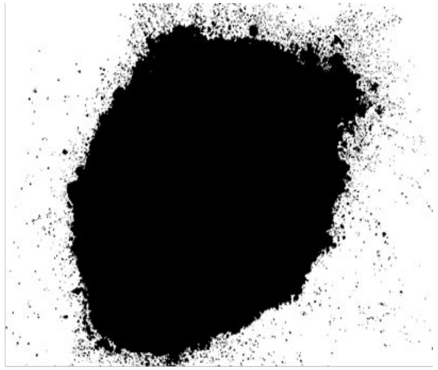
ELV-WP Flash Graphene Composites

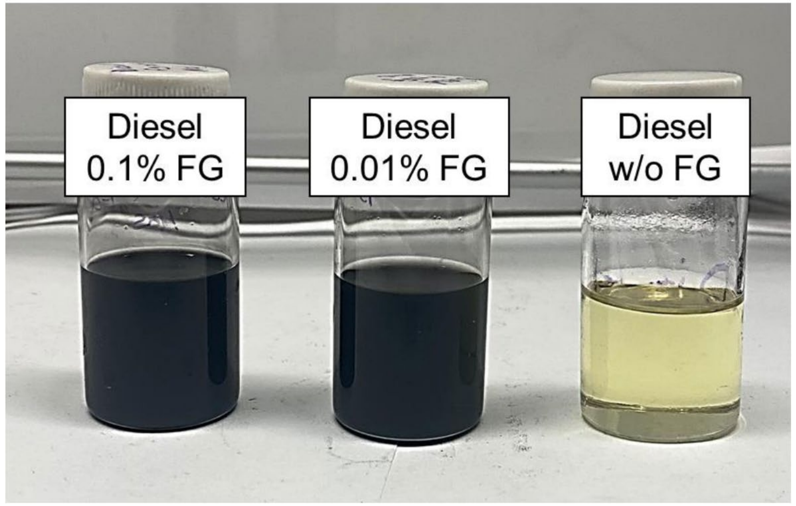
- We sent this graphene back to Ford Motor Company to use in polyurethane foams
- Circular use to convert from ELV-WP into a material that improves properties in cars
- Graphene already in Ford vehicles, but ELV-WP derived FG is a cheaper, greener alternative

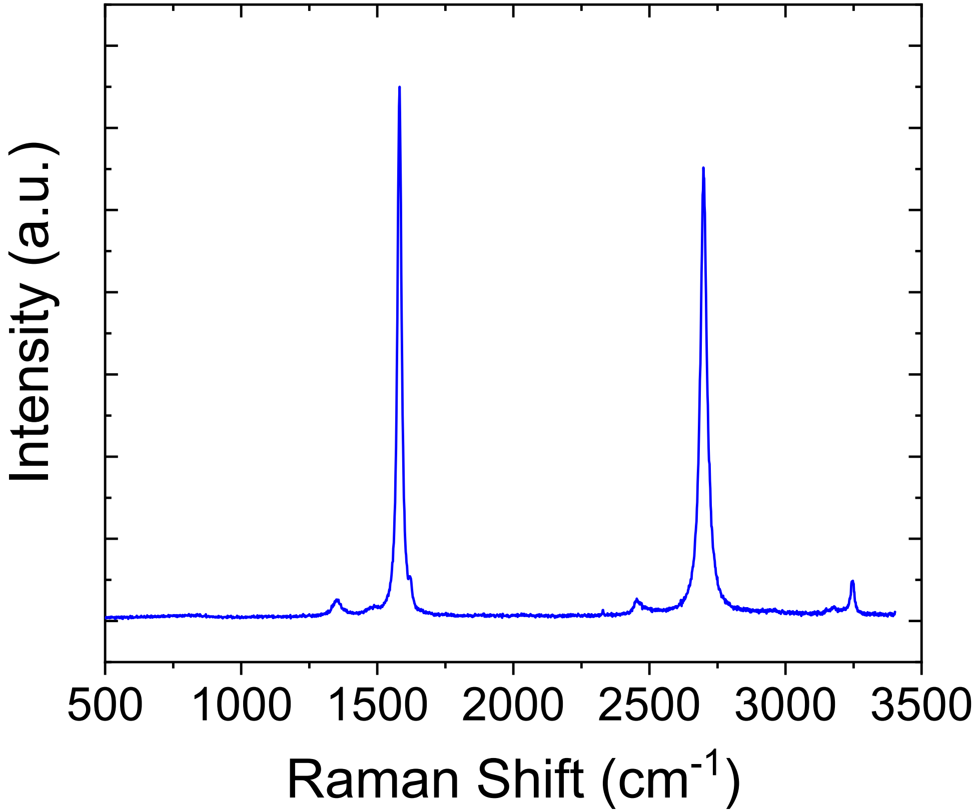




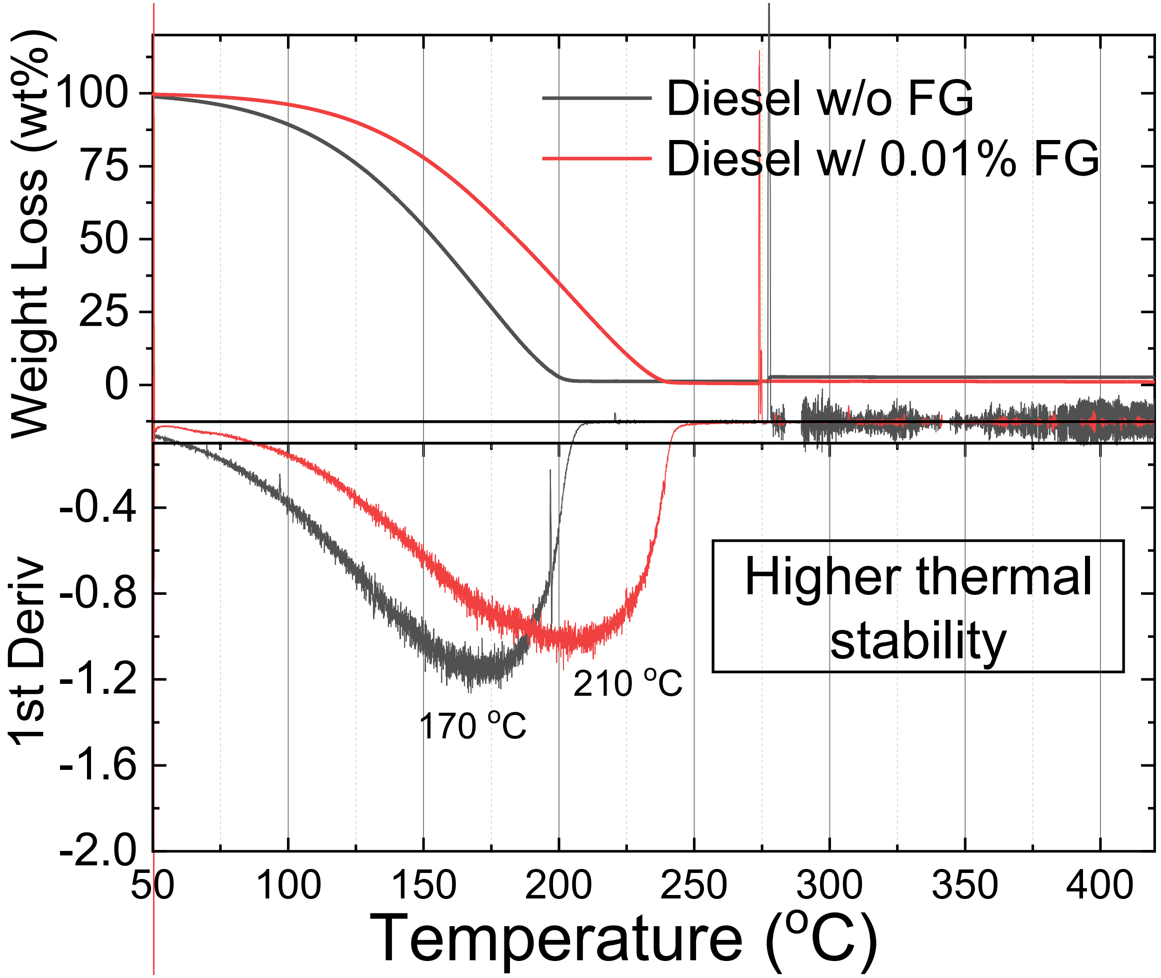
Spent motor oil soot converts well into high-quality graphene

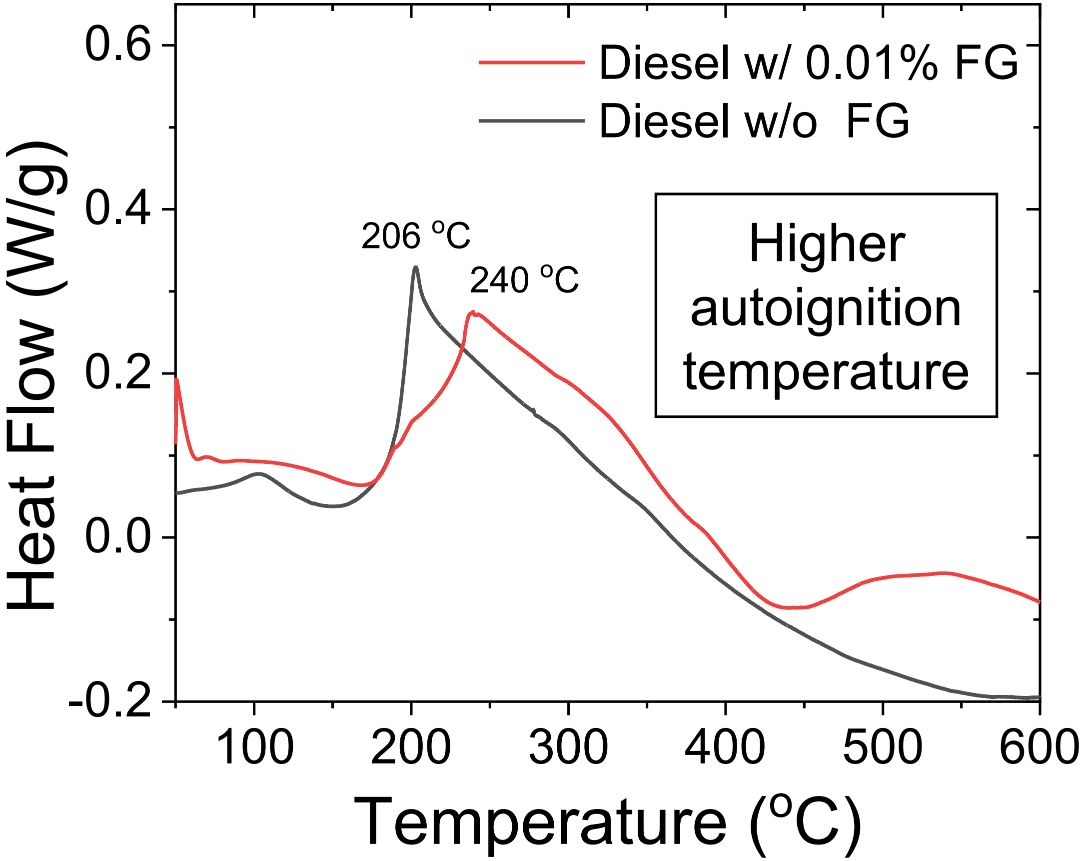




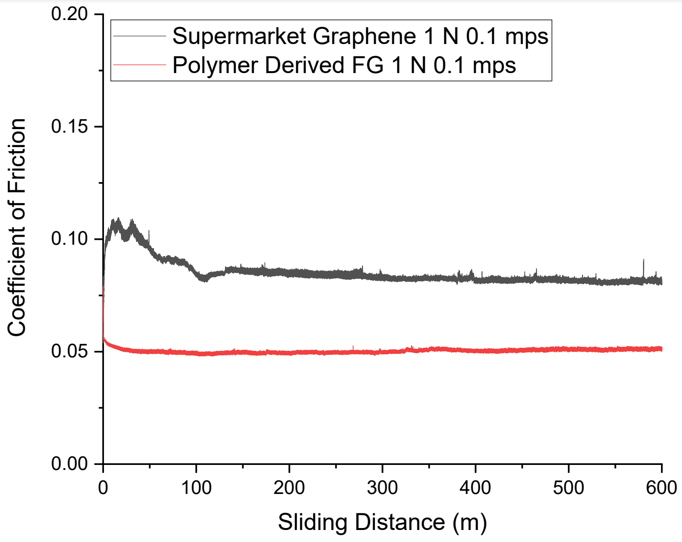


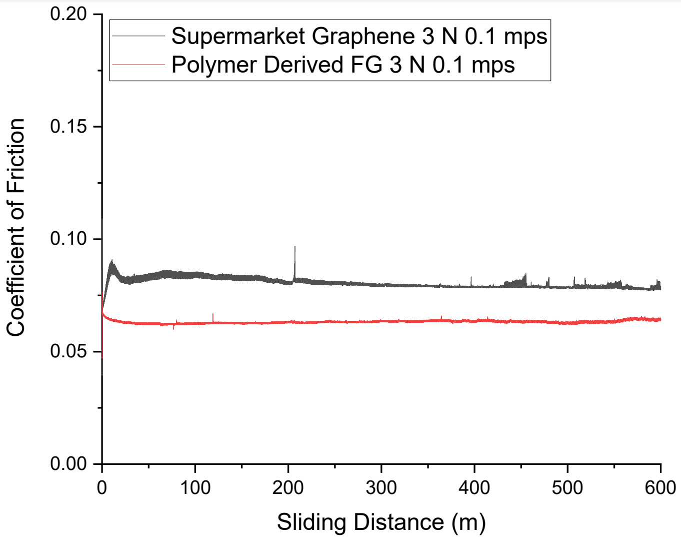
FG can be used as a fuel stabilizer

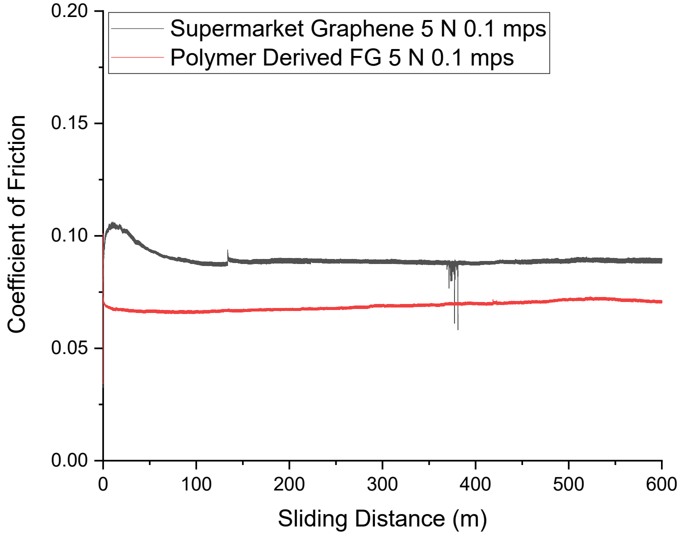


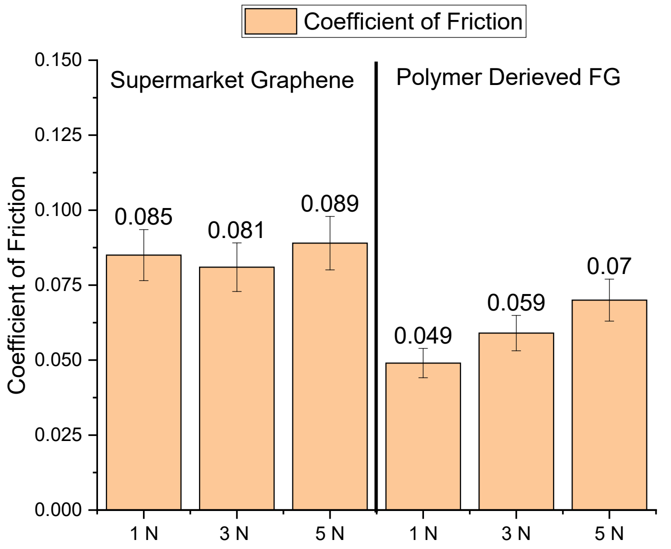


Friction performance comparison at 0.1 m/s sliding speed









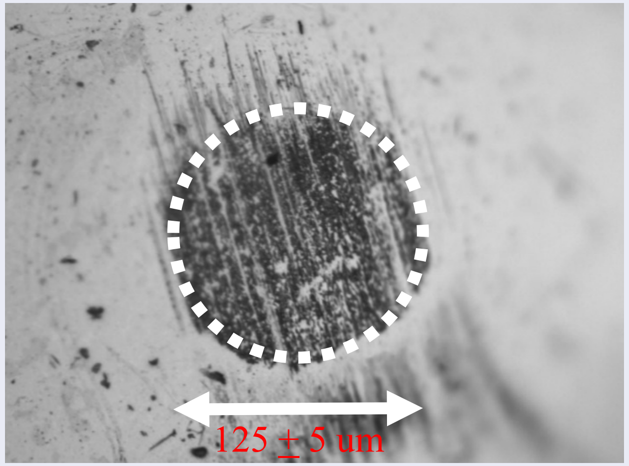
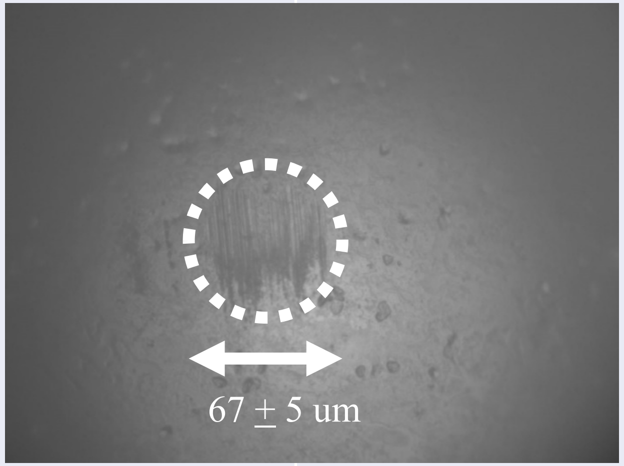
Test Conditions:

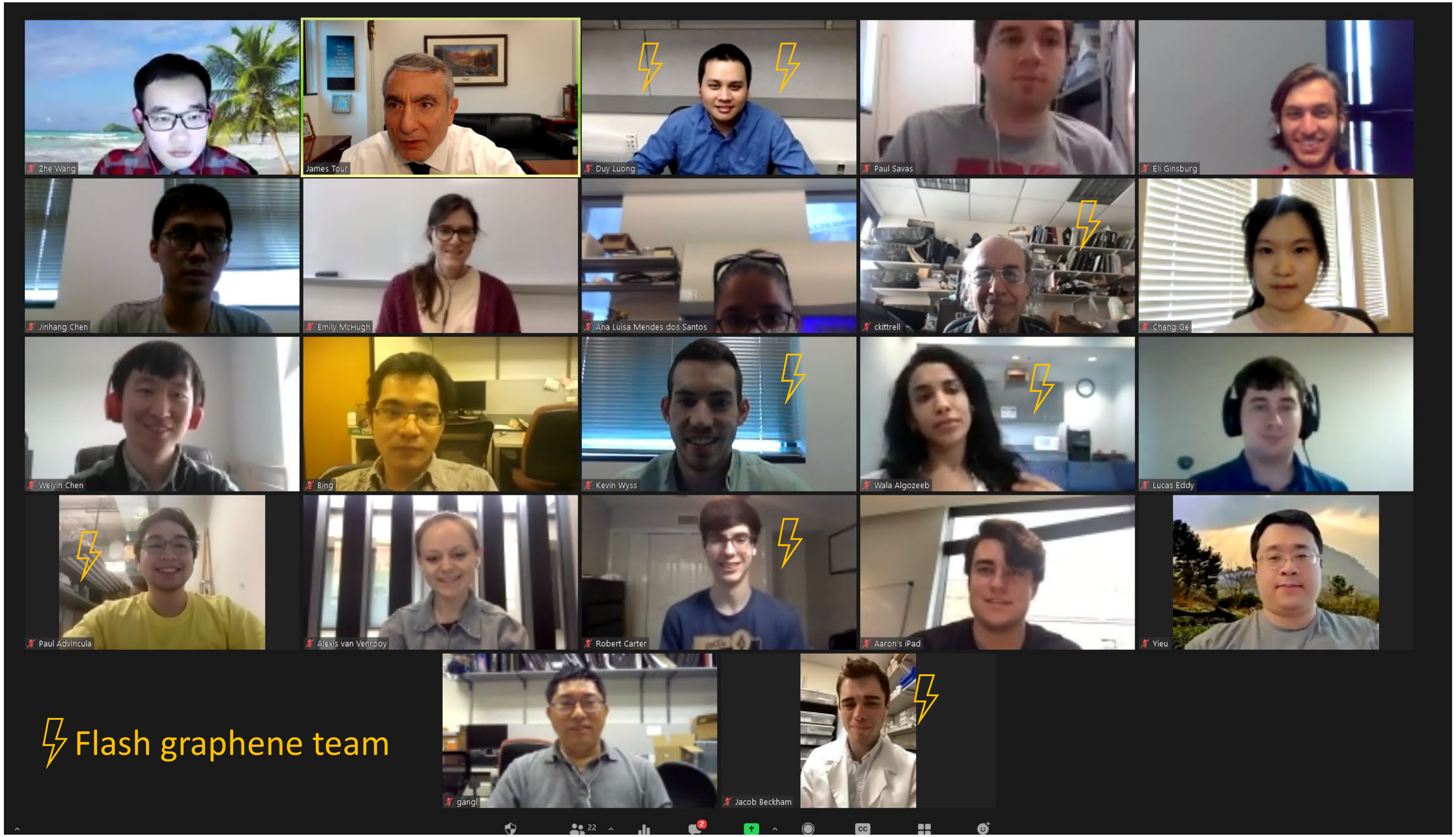
- PAO 9 base oil was dispersed with Supermarket graphene and Polymer derived flash graphene
- 0.25 g/l concentration
- Tests were carried out at 1,3,5 N at 0.1 m/s

- Polymer derived flash graphene displayed significantly lower friction than commercial Supermarket graphene

- Supermarket graphene is mechanically exfoliated + chemically treated graphene

Wear data comparison

Wear rate calculations (m^3/N-m)				
Type of Graphene ->	Supermarket Graphene		HDPE FG	
Test Load	0.1 mps	0.5 mps	0.1 mps	0.5 mps
5 N	7.0E-11	1.3E-9	5E-11	9.7E-11
Images				



Thanks to the DOE for support. DE-FE0031794

And Jason Hissam for patience during 2.5 months of lab closure and related 12 month delays