DE-FE0031794

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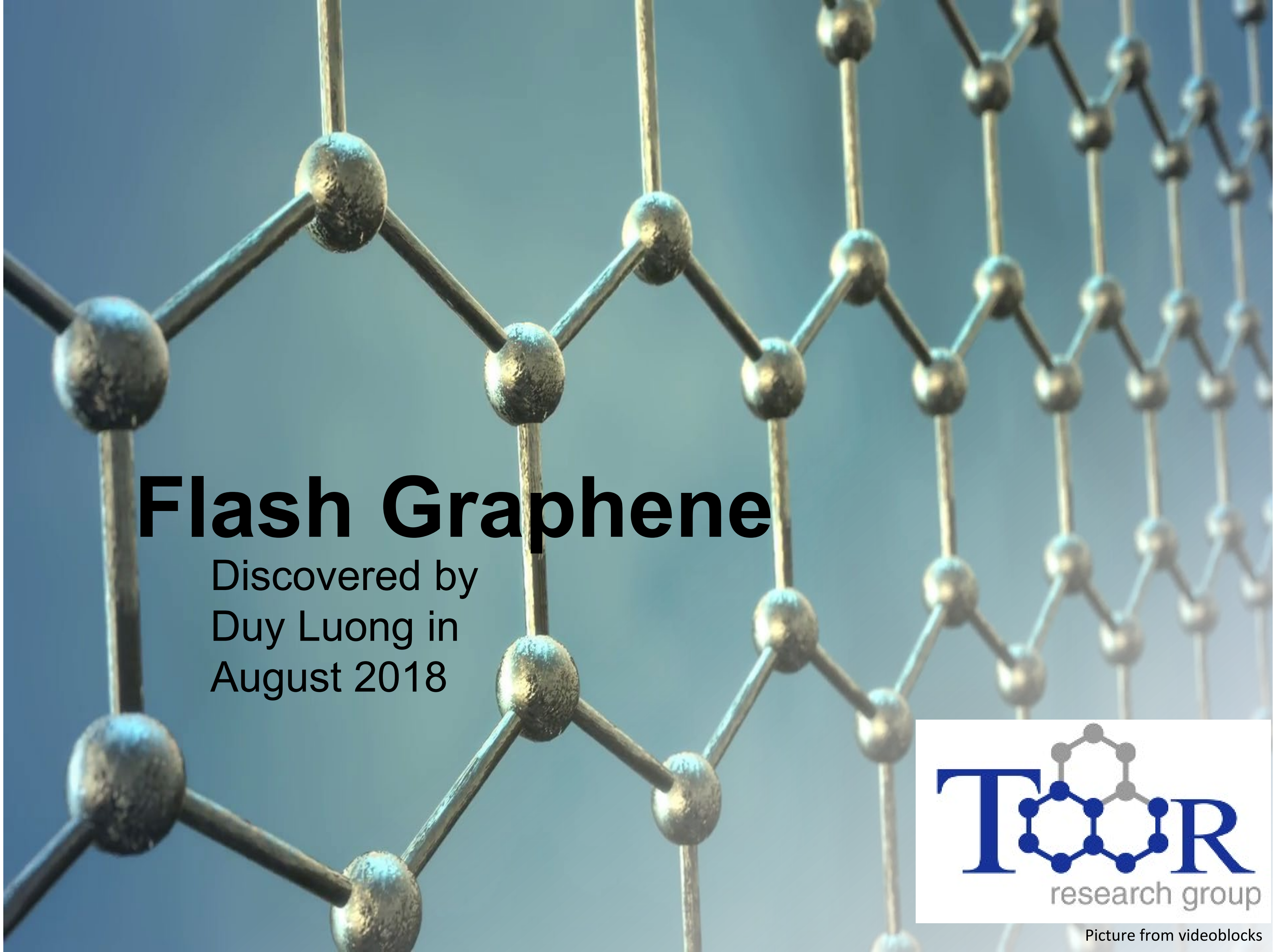
Virtual Review: 20 October 2020

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



Flash Graphene

Discovered by
Duy Luong in
August 2018

TOUR
research group

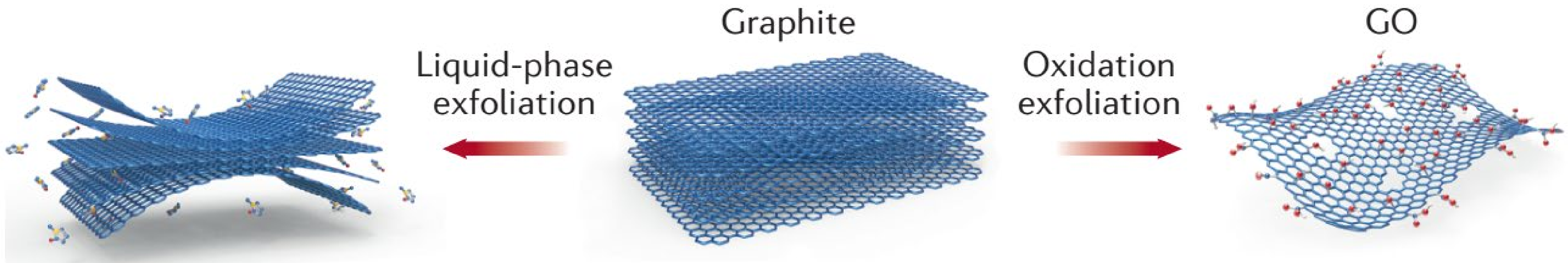
Picture from videoblocks

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 Synthesis



Electrochemical Exfoliation
Cons: 1. Impurities 2. Quality control hard

Chemical Exfoliation
Cons: 1. Highly defective product 2. Harmful by product
3. Poor quality product 3. Complex synthesis

Top down

Bottom up

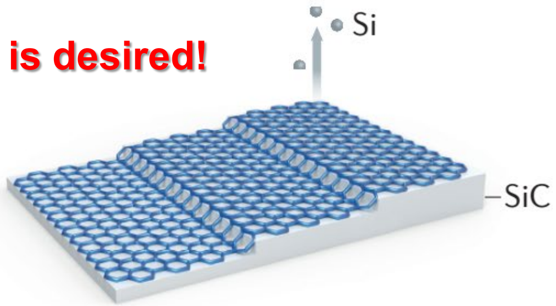
Top down

Bottom up

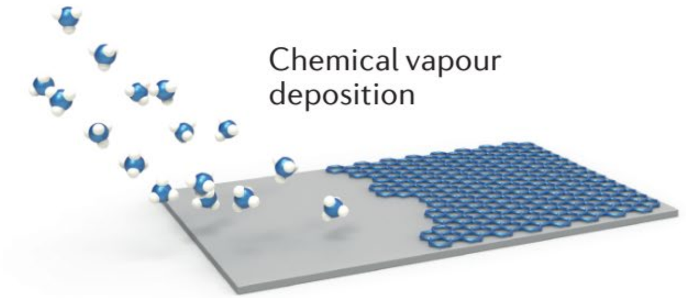
Limitations for industrialization:

1. **Low product yield**
2. **Environmental contamination**
3. **Time-consuming**
4. **Transfer & Integration**

A new method is desired!



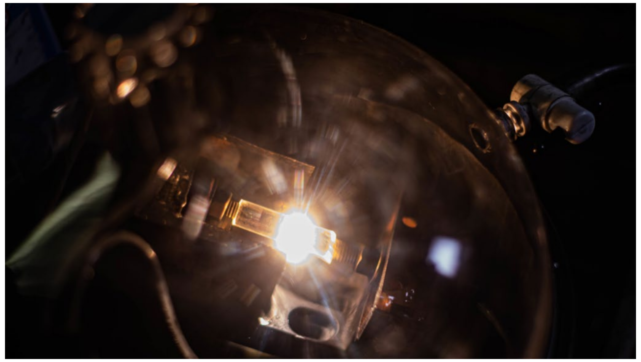
Epitaxial Growth
Cons: 1. Non-uniform product 2. High temperature required
3. Time-consuming process 4. Low-yield 5. Hard transfer

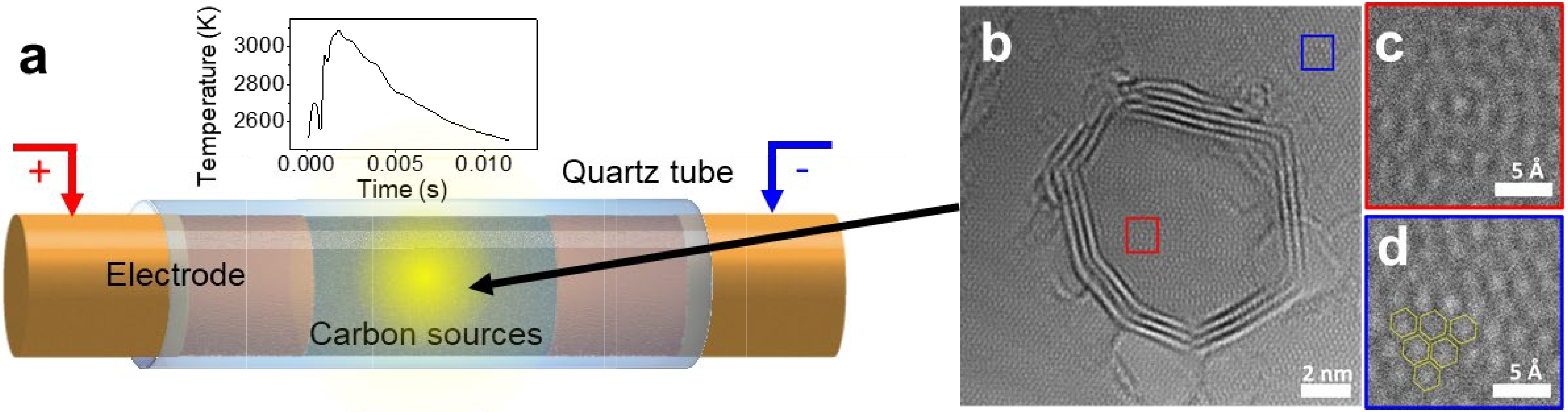


Chemical Vapor Deposition
Cons: 1. High temperature required 2. Quality control hard
3. Time-consuming process 4. Hard transfer 5. Harmful byproduct

DOI: 10.1038/s41570-017-0100

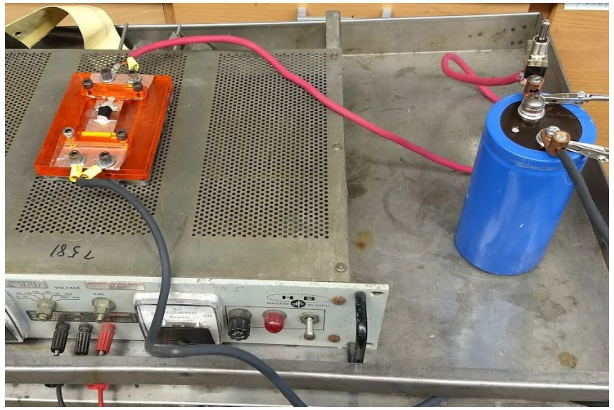
Flash Graphene Synthesis



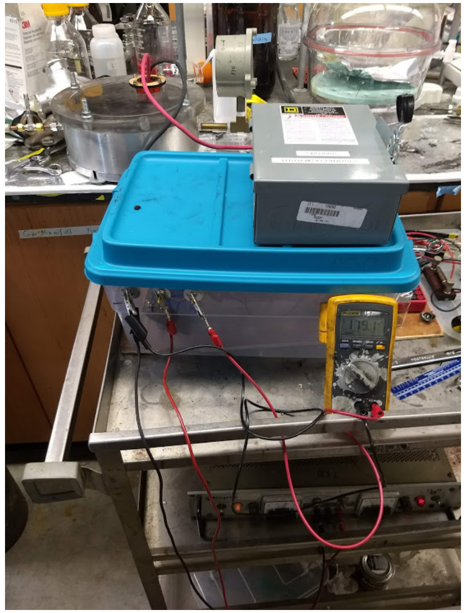


Carbon materials are converted efficiently into high quality turbostratic graphene

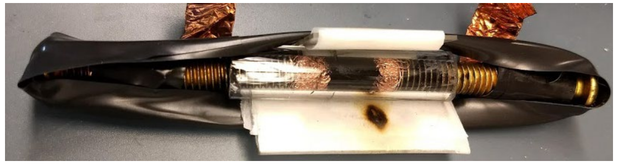
Flash Unit Progression



FJH Beta



FJH V0

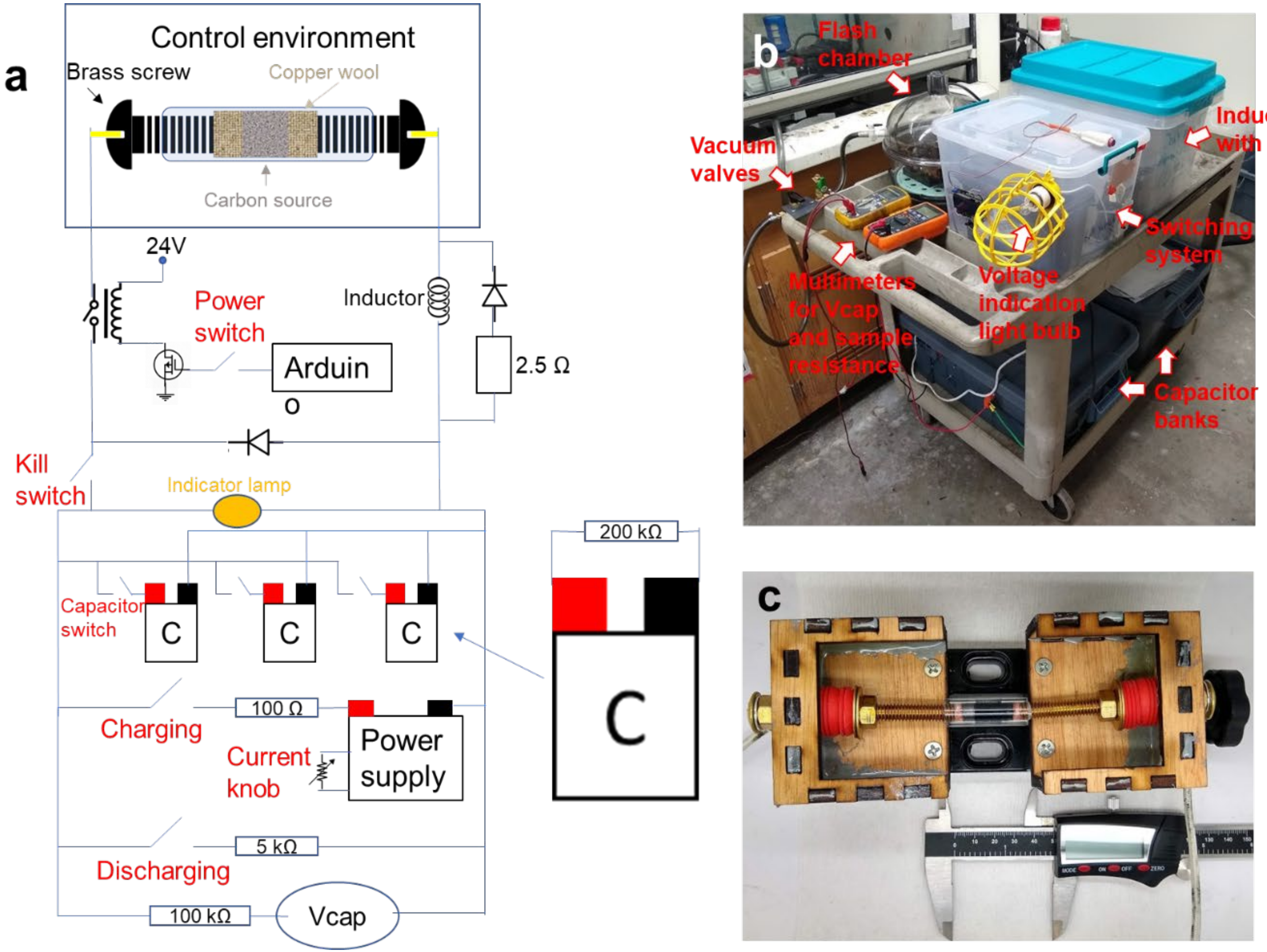


FJH V0 sample

FJH V1

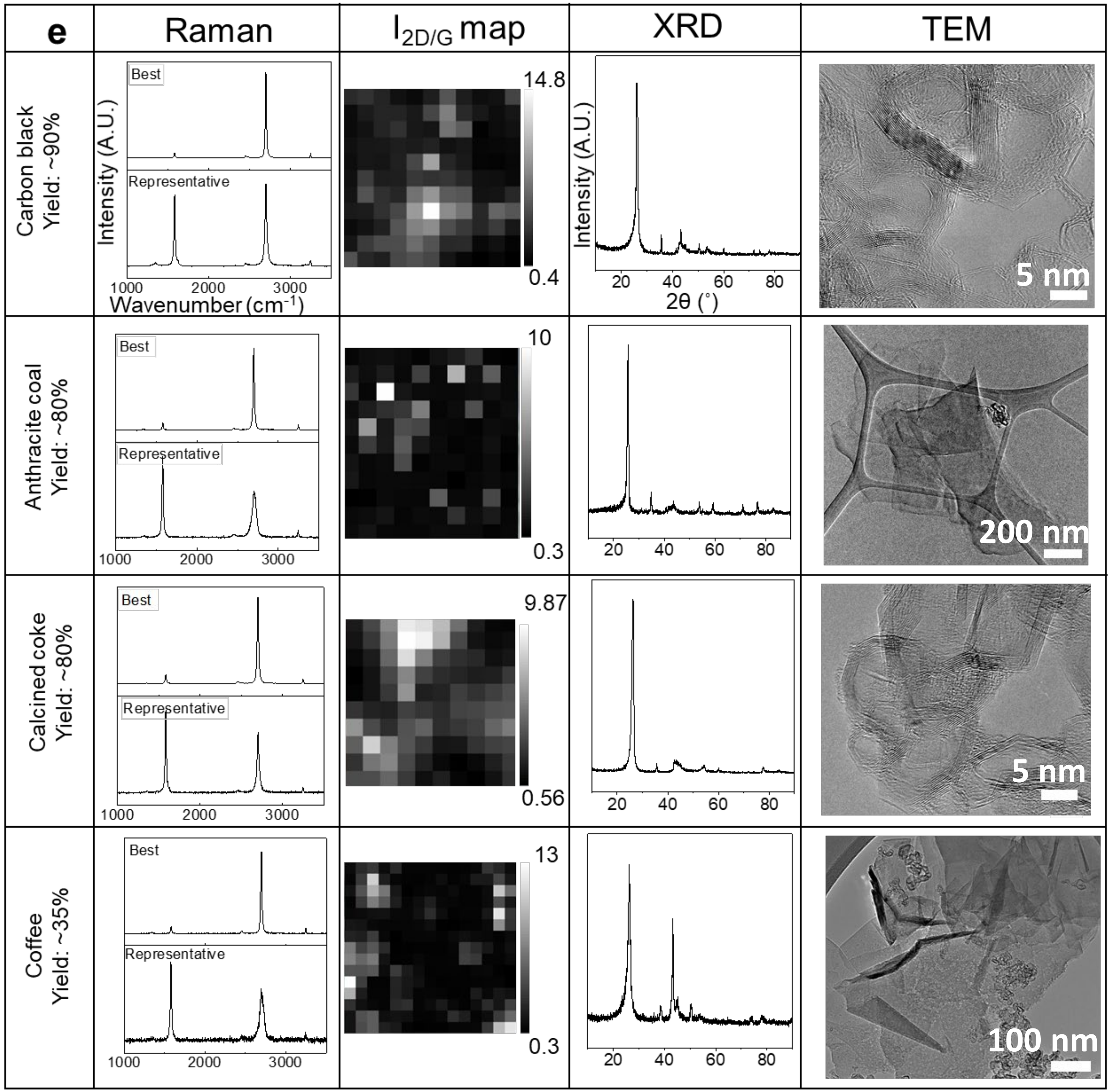
FJH V1
sample

FJH V2.1



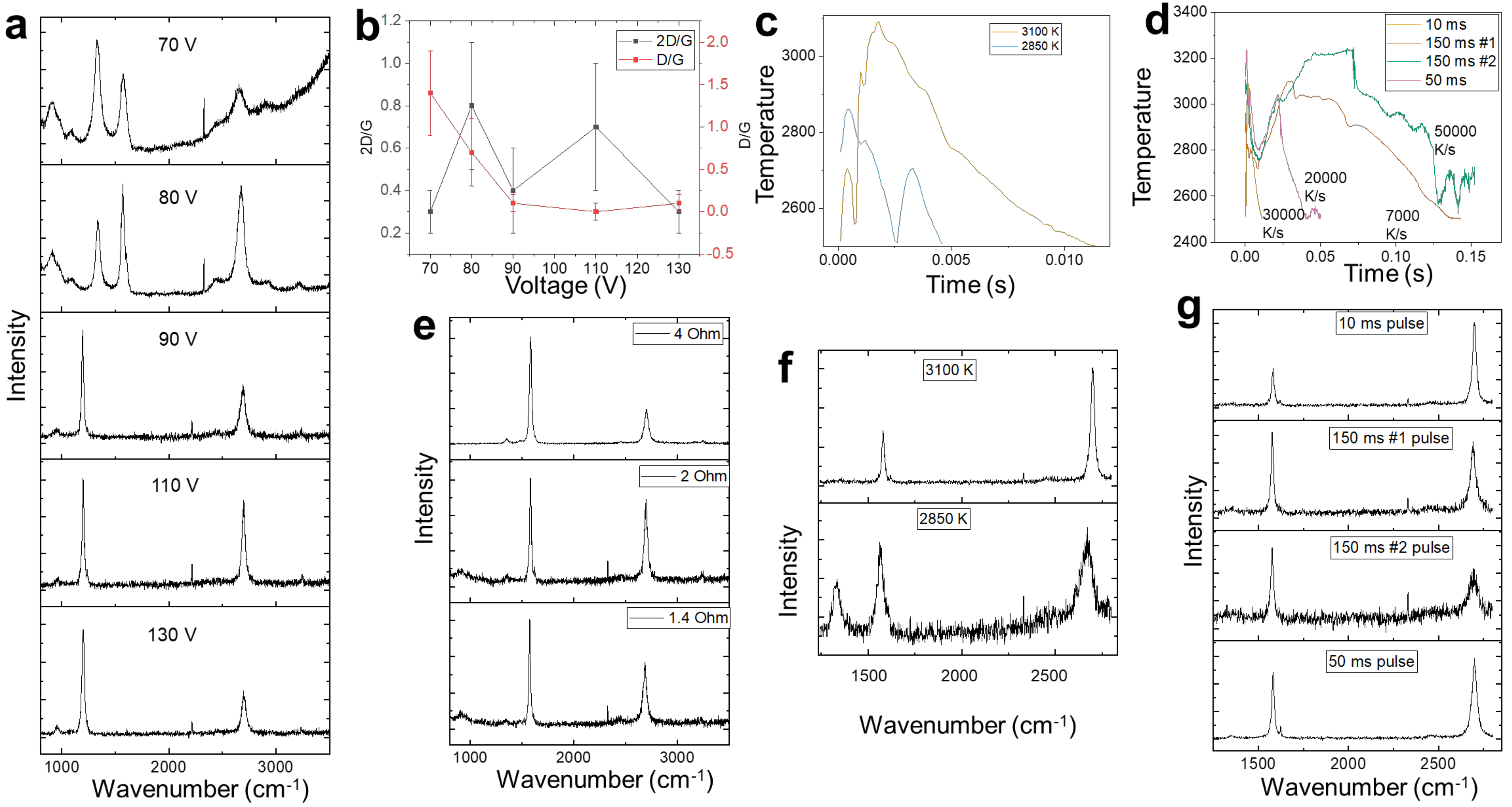
Flash Graphene Apparatus

Flash Graphene Characterization

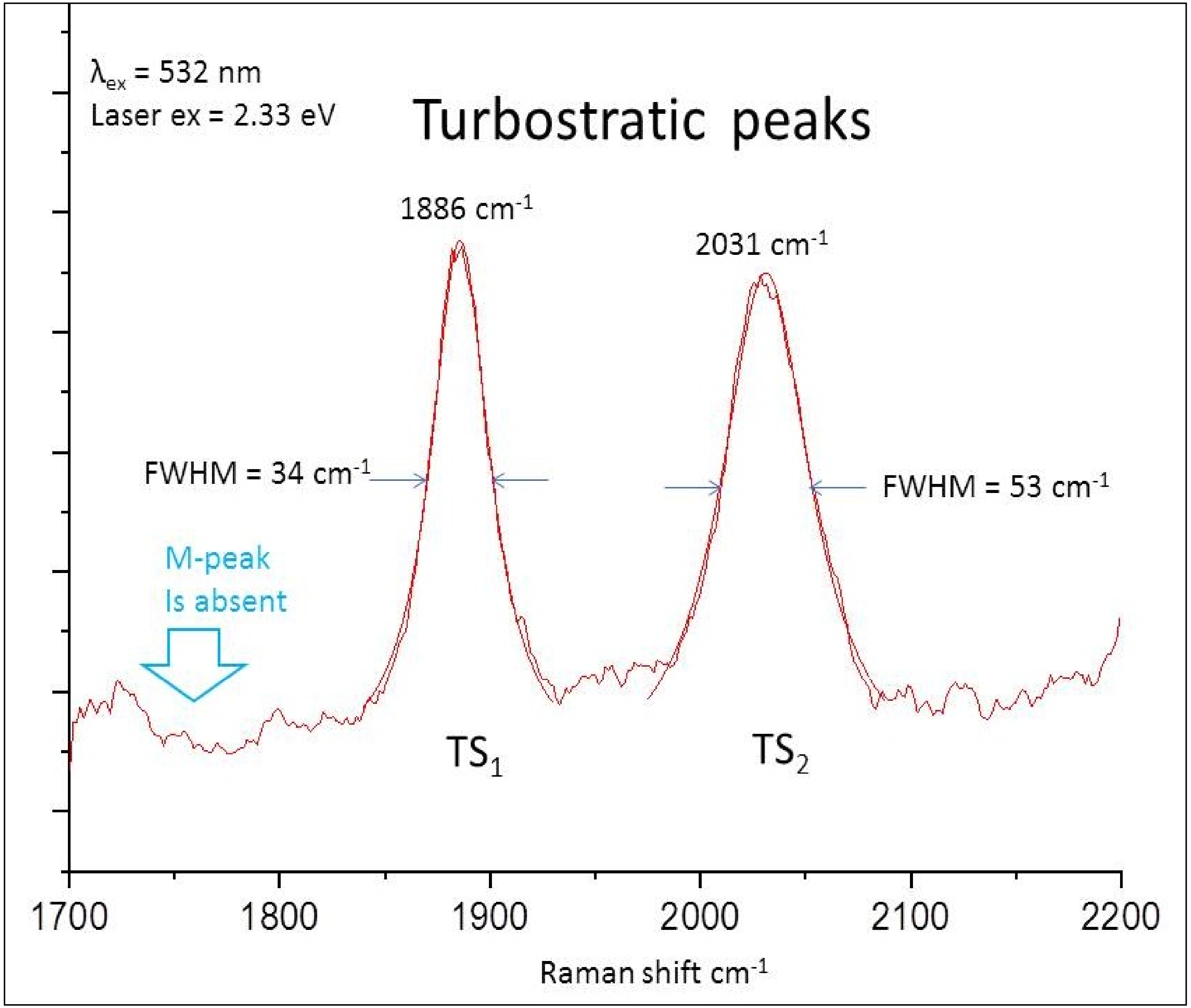


- Various carbon materials can be converted into graphene.
- Graphene quality is high.
- Graphene is turbostratic which facilitates dispersion in composites
- $35/ton in electrical energy costs

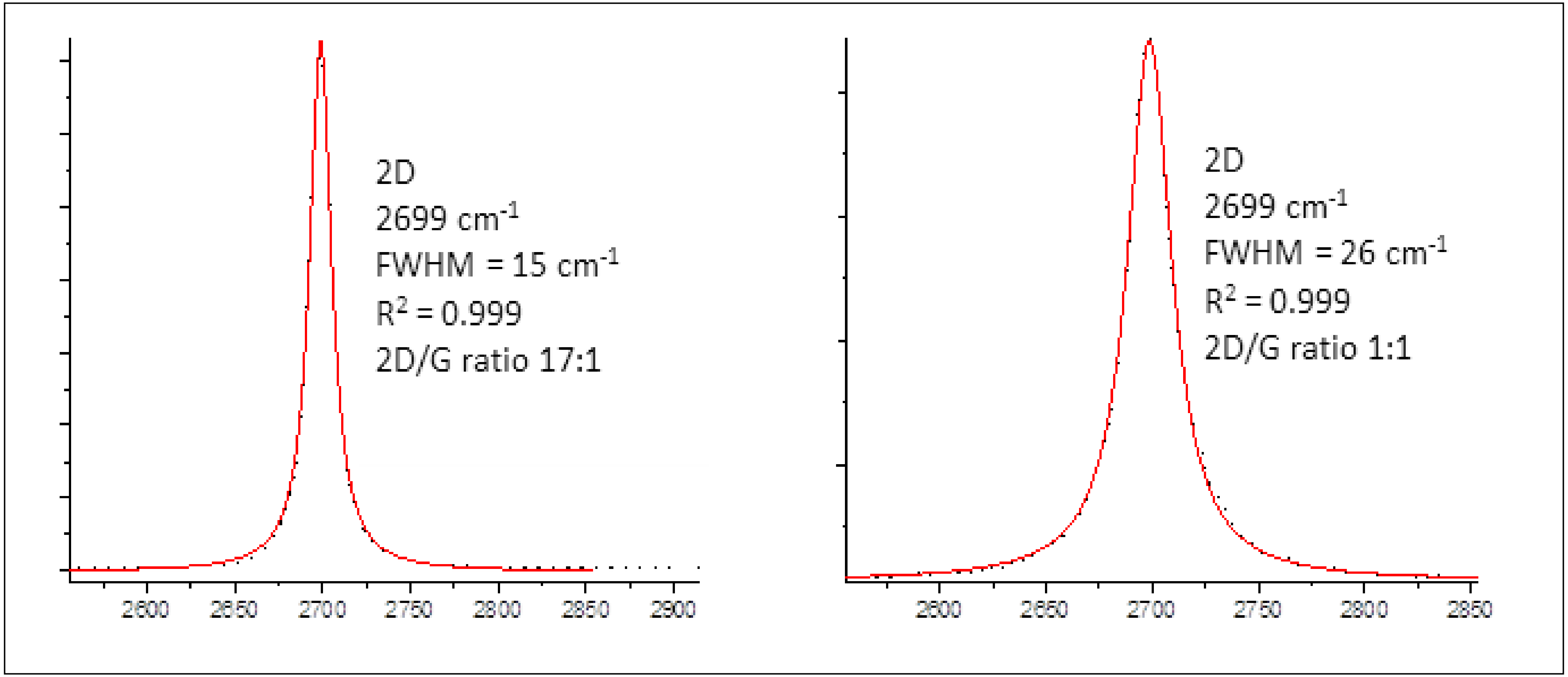
Time Temperature Dependence



- 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

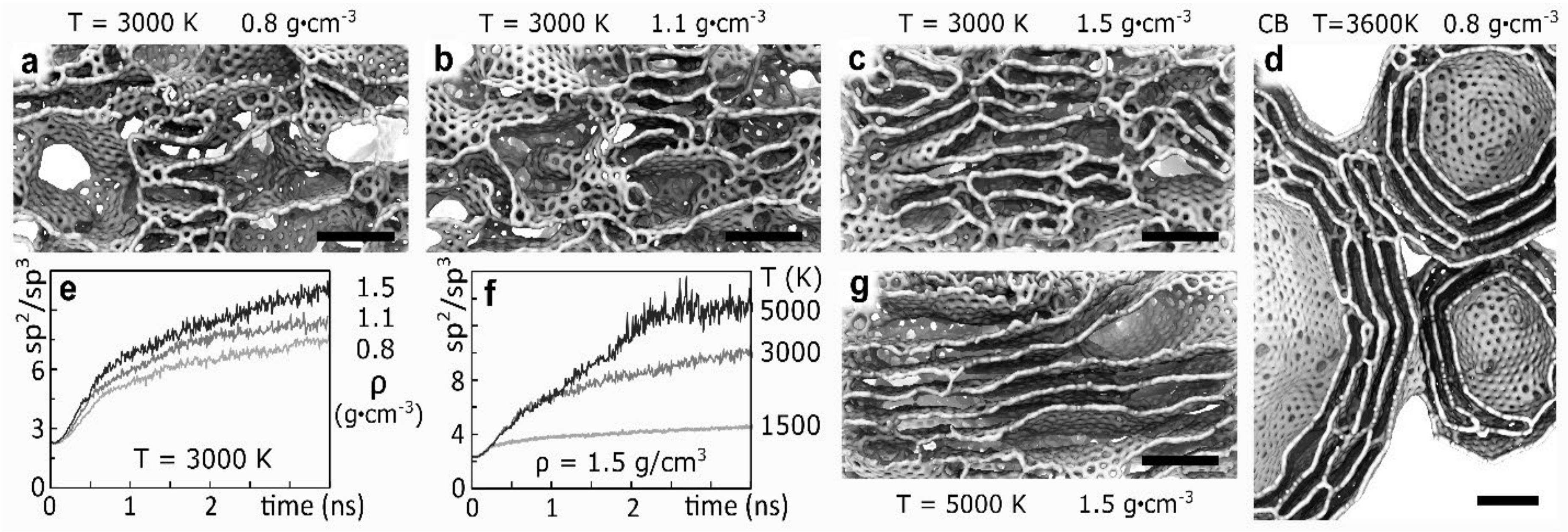


Turbostratic peaks in the Raman spectrum of CB-FG. $I_{G/TS1}$ ~30. Lorentzian fit is shown as a superimposed smooth line. The R-squared is 0.994 for TS_1 and 0.99 for TS_2. These excellent fits indicate the high quality of the FG and the unmistakable presence of these Raman lines are attributable to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



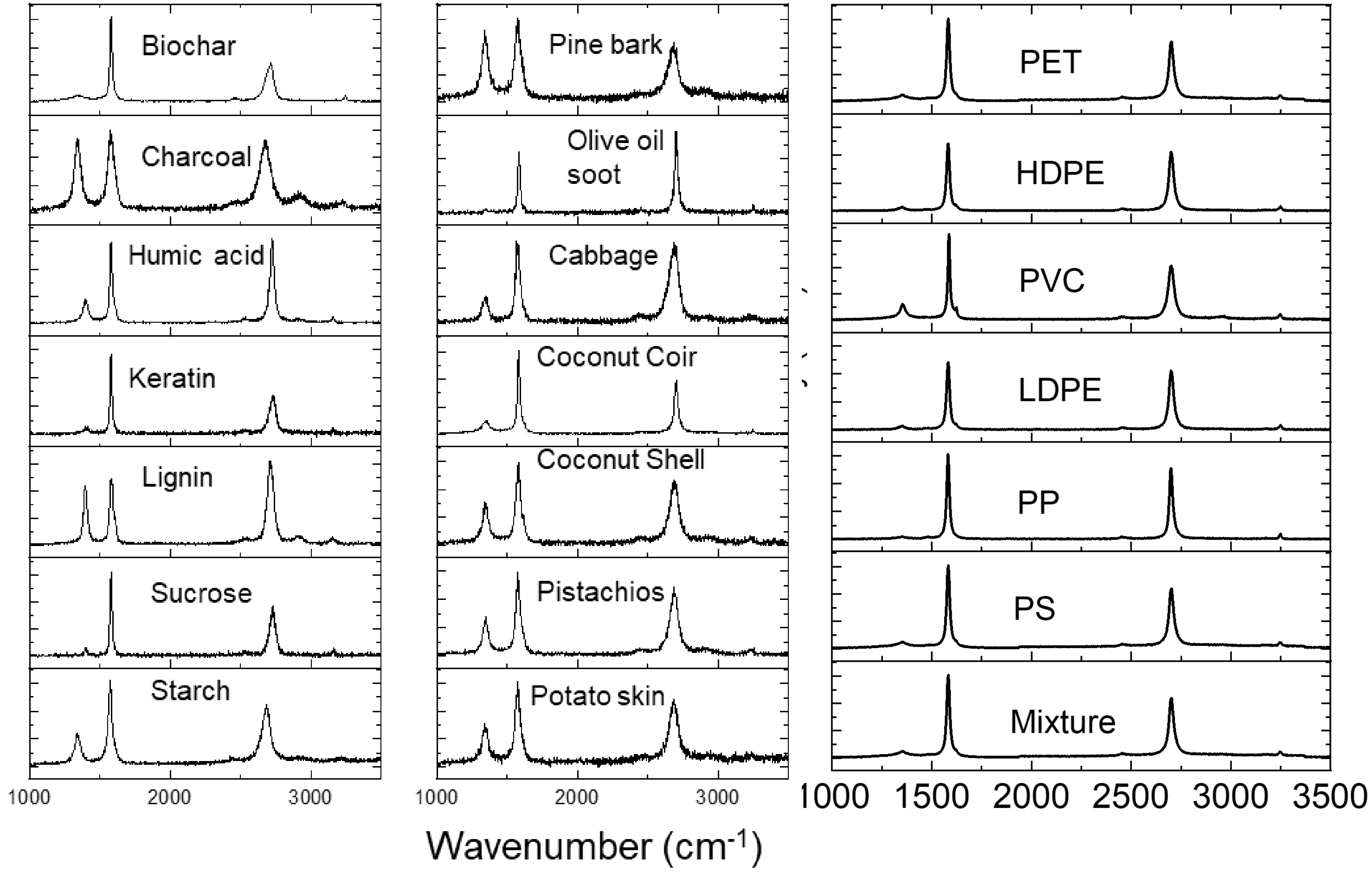
2D peak in the Raman spectrum of CB-FG. Left: best point in CB-FG, right: representative point in CB-FG. Both peaks exhibit nearly a perfect Lorentzian line shape. The black dots are the theoretical line shape. The R^2 for the correlation is 0.999 for both peaks. This is indicative of a fully conical Dirac cone at the K-point. The exceptionally large $I_{2D/G}$ is also indicative of multilayer turbostratic graphene, as several researchers point to an increasing $I_{2D/G}$.

Simulations



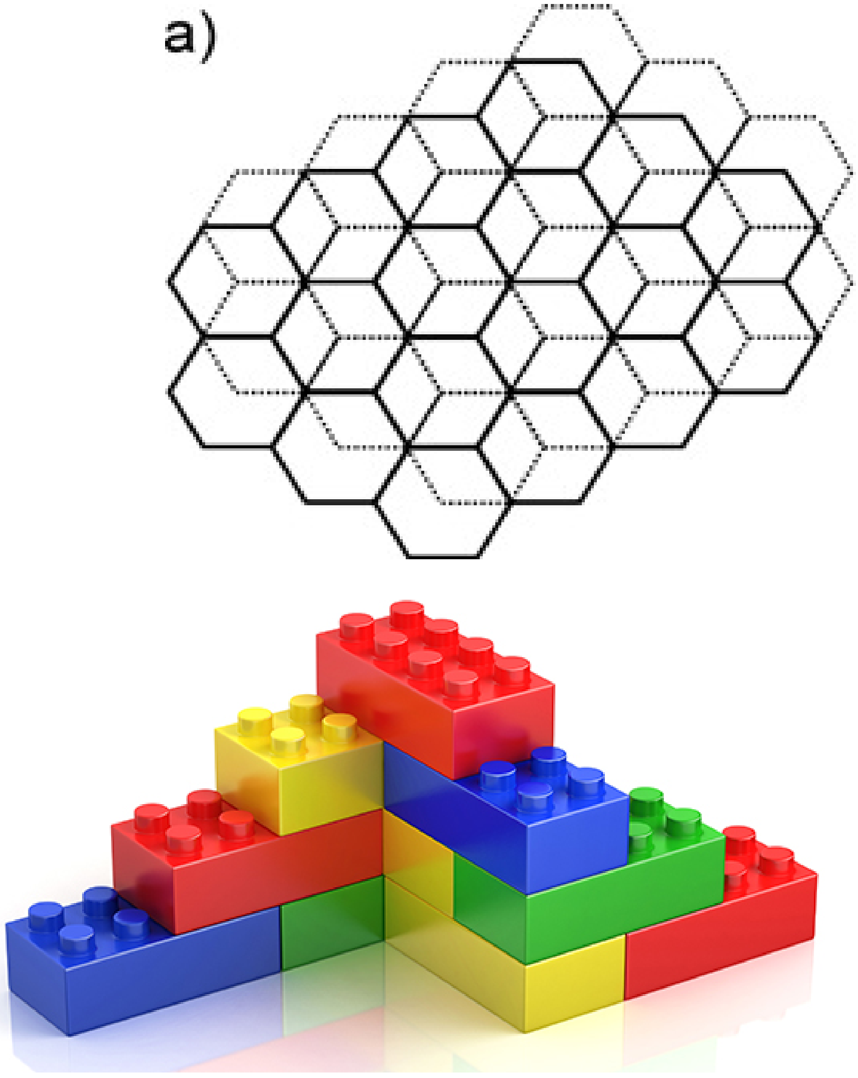
Molecular dynamics (MD) simulations of structures with various characteristics (such as micro-porosity, misalignment, and size of graphitic domains) kept at a given temperature range (1500 to 5000 K) for a prolonged time (up to 5×10^{-9} s, with NVT thermostat). Sample structure after annealing at 3000 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.

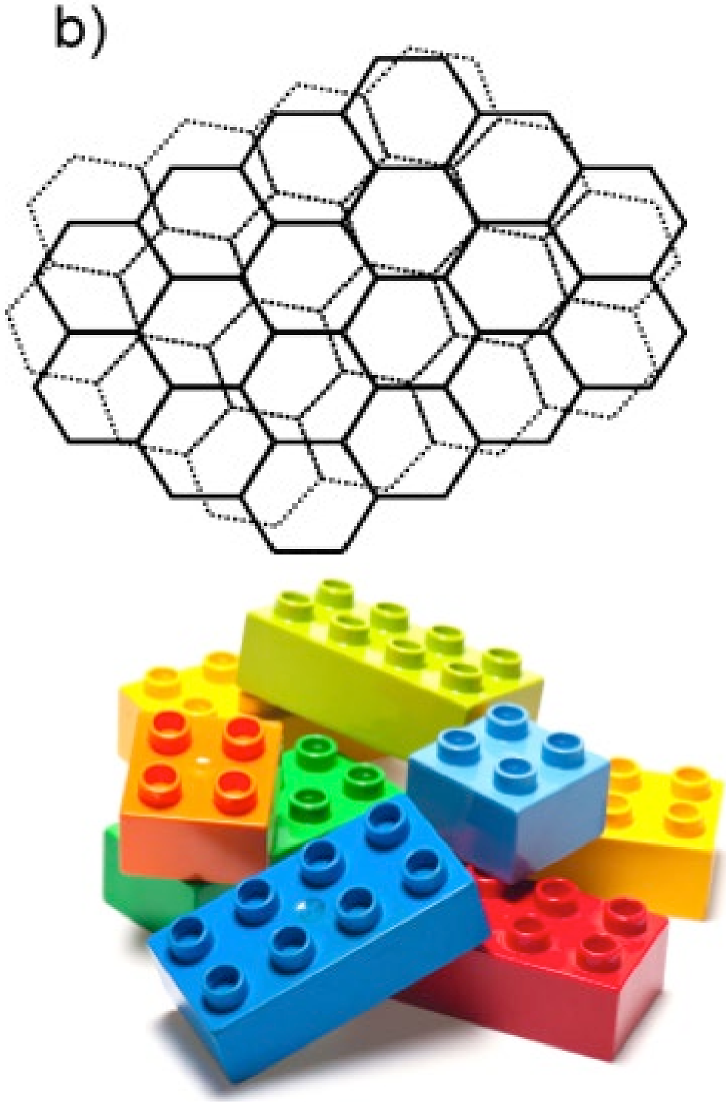
Flash graphene from “any” solid carbon source



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.

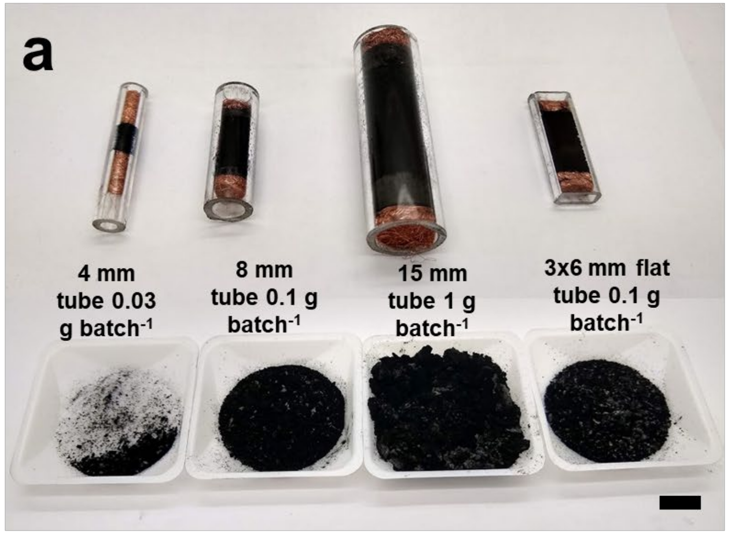
a) AB-stacked (Bernal) vs. b) turbostratic graphene

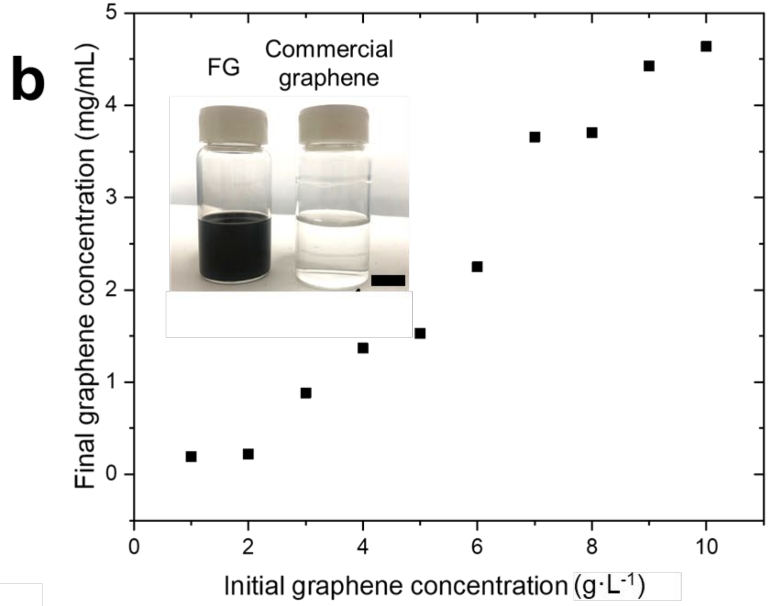


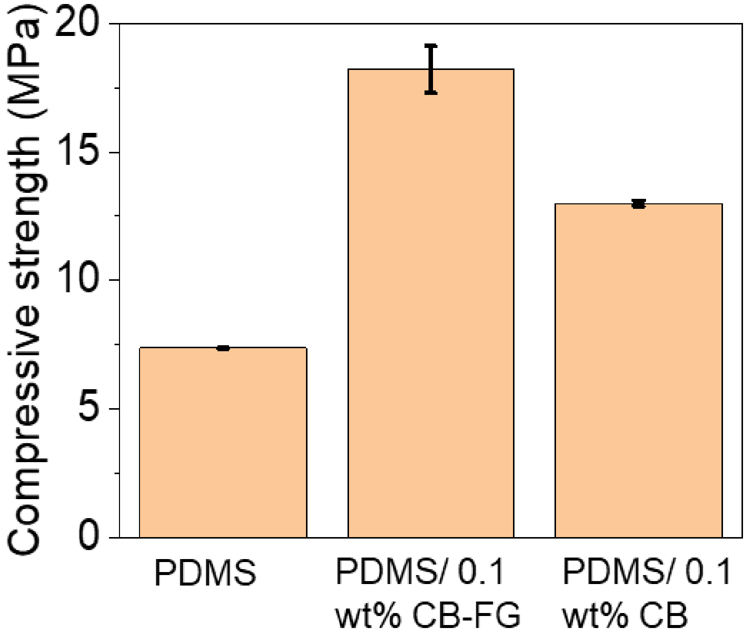


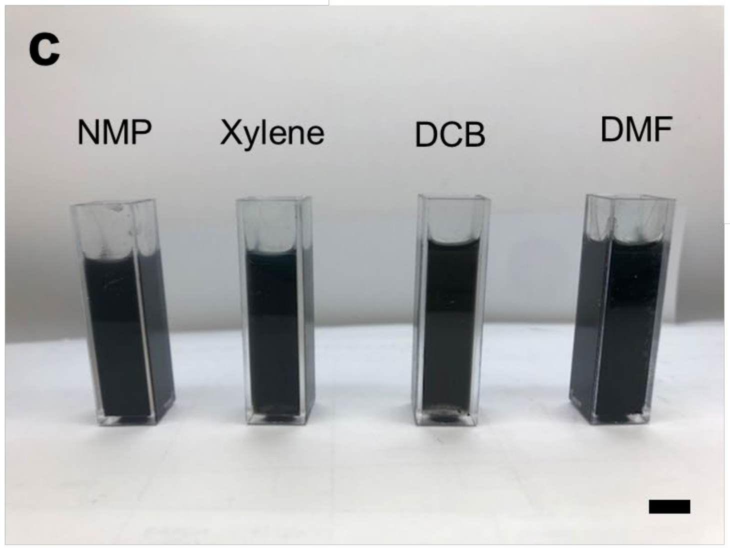
https://doi.org/10.1002/smll.200901173

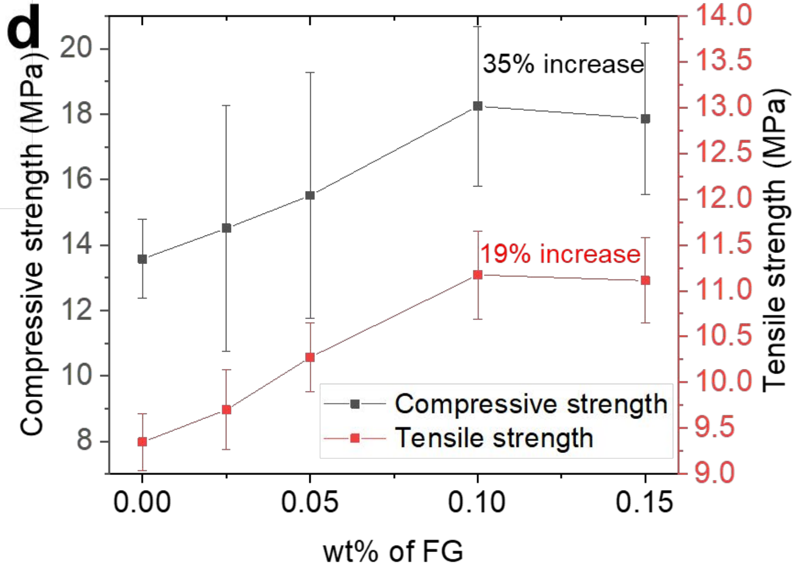
Laboratory Scale-up FJH V2.1



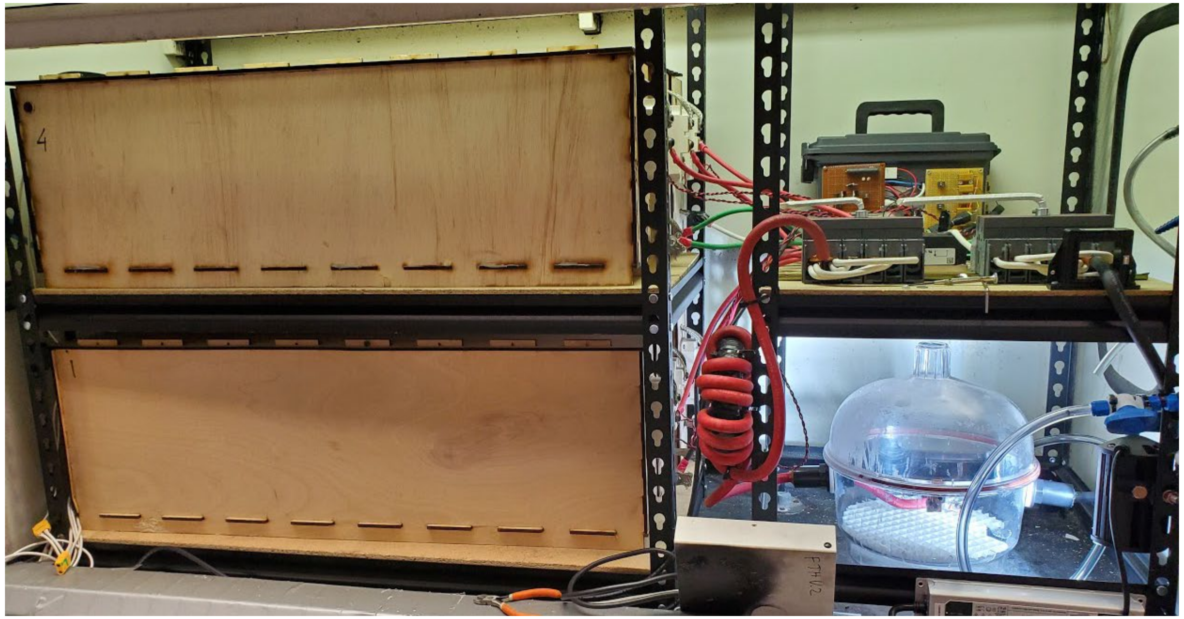


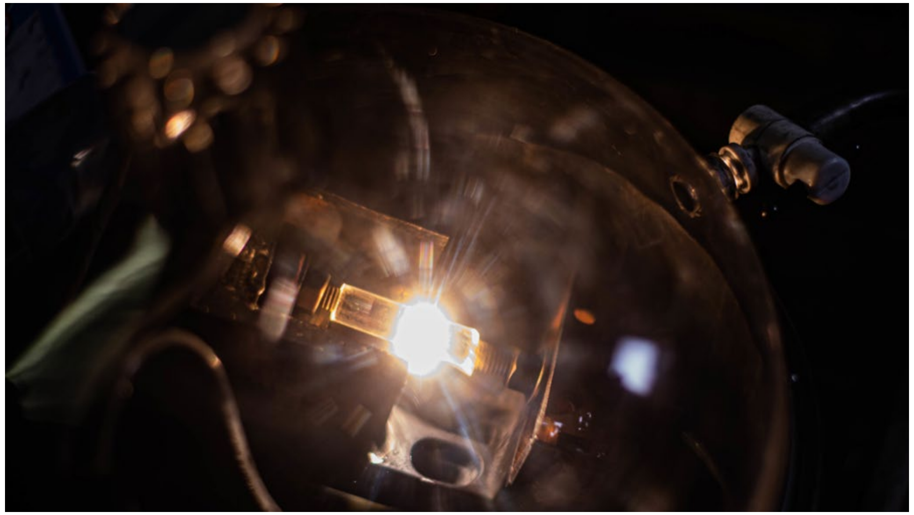


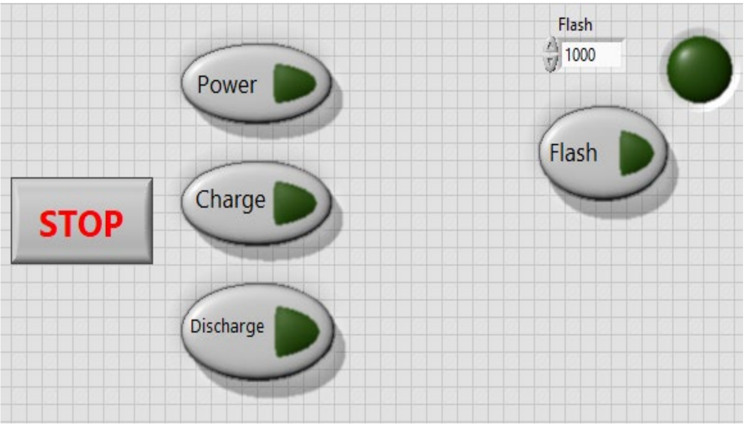




FJH 5.0







Graphene can be used for so much

RICE

www.universalmatter.com

1 kg/day prototype will be GMP-approved graphene for medical purposes

FJH 5.0 Pill and Powder flashing

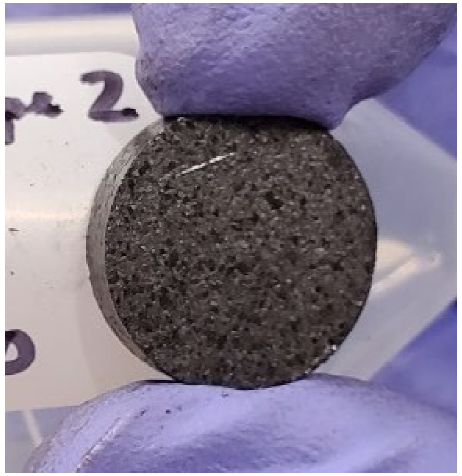
- Powder flashing
- Flashing powder inside quartz tube
- Pros
- Less volatile in feedstock lead to ease of optimization
- Cons
- Depends on a holder tube that is less attractive for scale up

- Pill flashing
- Flashing compressed pill in free form
- Pros
- Independent of a holder tube, desirable for scale up system
- Cons
- Need to find good binder with less volatiles
- Electrical contact need to be precise

FJH 5.0 flashing 1 g pill

- Metallurgical coke (MC) and raw green petroleum coke (GPC) are mixed and pressed into pill. GPC acts as binder while MC acts as conductor. Both are graphene source
- GPC and MC need to have the same size to make consistent pills
- Too large grain size yields pill inconsistency
- Pills are compressed with 15 mm die under 5 tons pressure

Sieve #20/30 pill



Sieve #50/70 pill

FJH 5.0 pill optimization

MC/GPC	#20-30 (0.6-0.84 mm)	#30-50 (0.3-0.6 mm)	#50-70 (0.21-0.30 mm)
50/50	Flashable	Flashable	Flashable
30/70	Inconsistent	Inconsistent	Inconsistent
70/30	Pill break	Flashable	Flashable

9 pills compositions

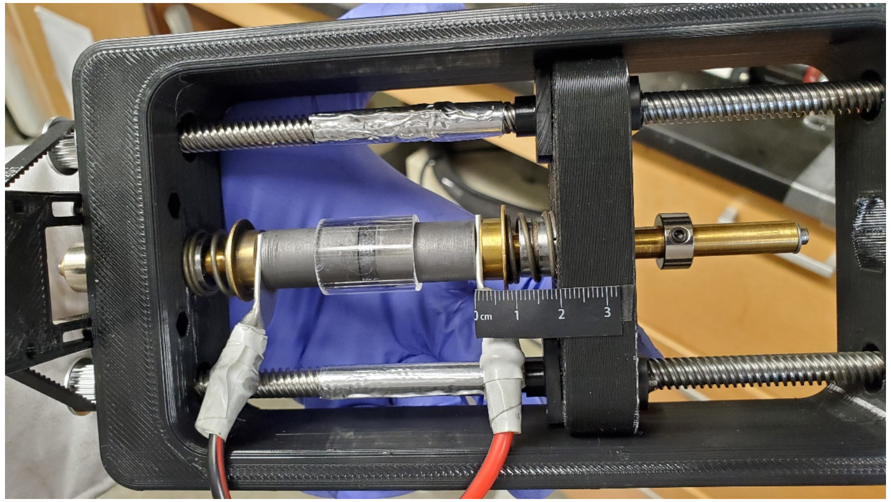
✖

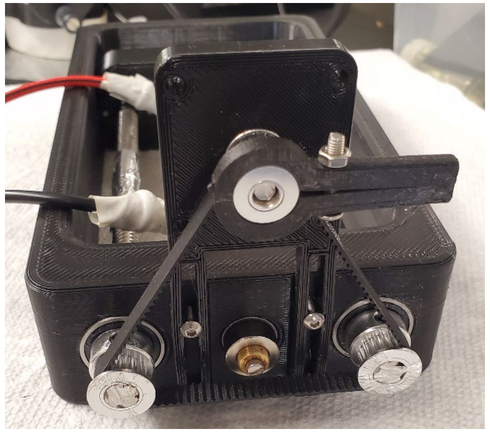
Voltage	Frequency (Hz)/ duty cycle (%), ON/OFF (ms)					
	200/10 0.5/4.5	200/20 1/4	200/50 2.5/2.5	1000/10 0.1/0.9	1000/20 0.2/0.8	1000/50 0.5/0.5
160	20-30%	30-40%	Lost form	10-20%	20-40%	20-40%
200	30-40%	Lost form	Lost form	30-40%	30-40%	Lost form

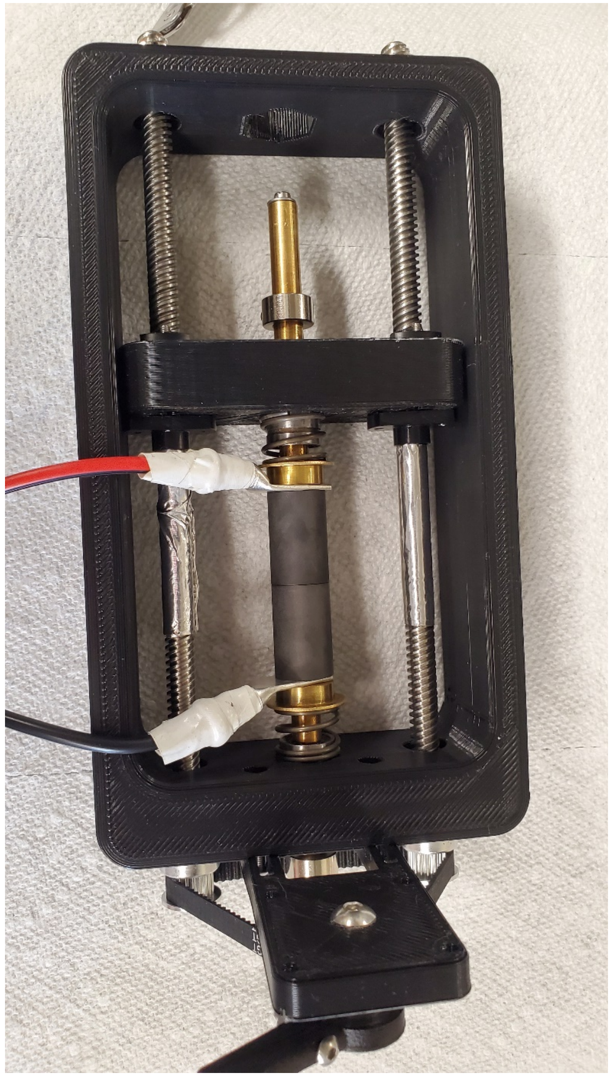
12 basic flashing parameters (50/50 #30-50 sample)

FJH 5.0 flashing 1 g pill

- Flashing jig for pill

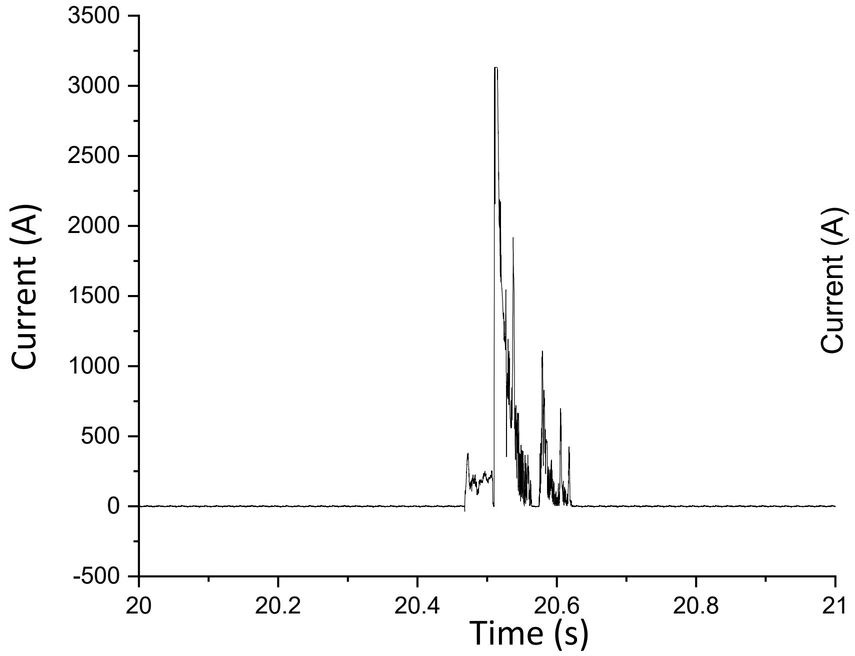




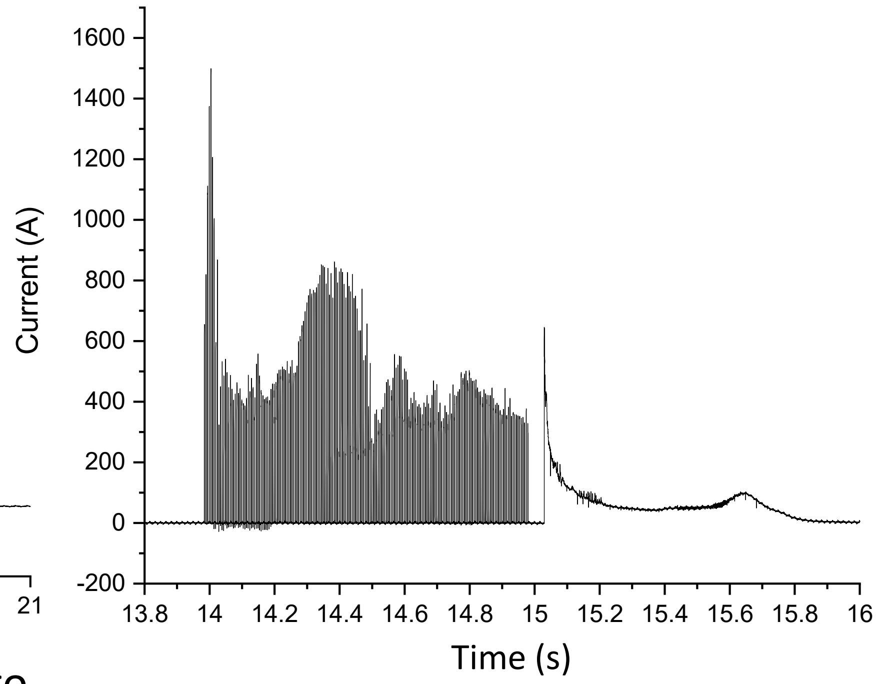


Variable Frequency Drive flashing

- Using pulse width modulation, we can turn DC flashing into AC flashing
- The result is homogeneous and controllable flash
- Raman shows graphene yield > 80%



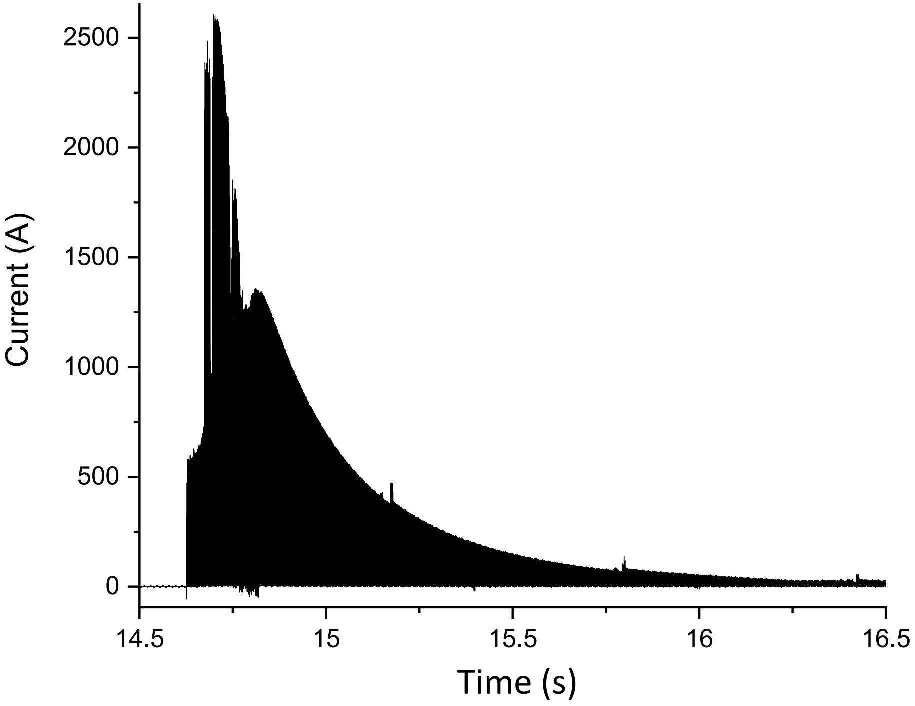
Simple DC flash brings the current up to more than 3000 A and result in a less controllable reaction.



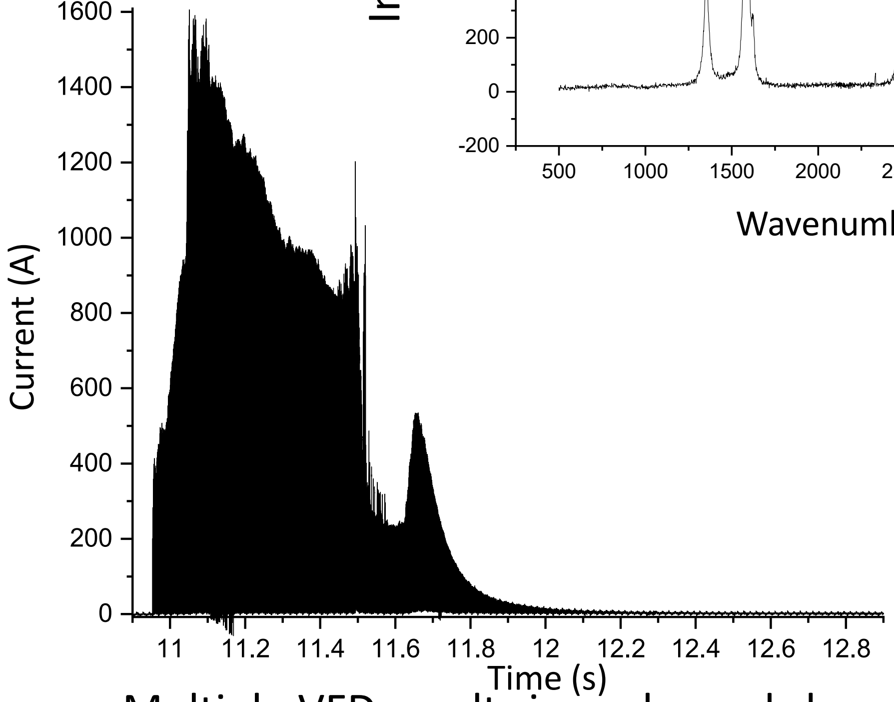
VFD flash allows controllable current and stop the chain reaction.

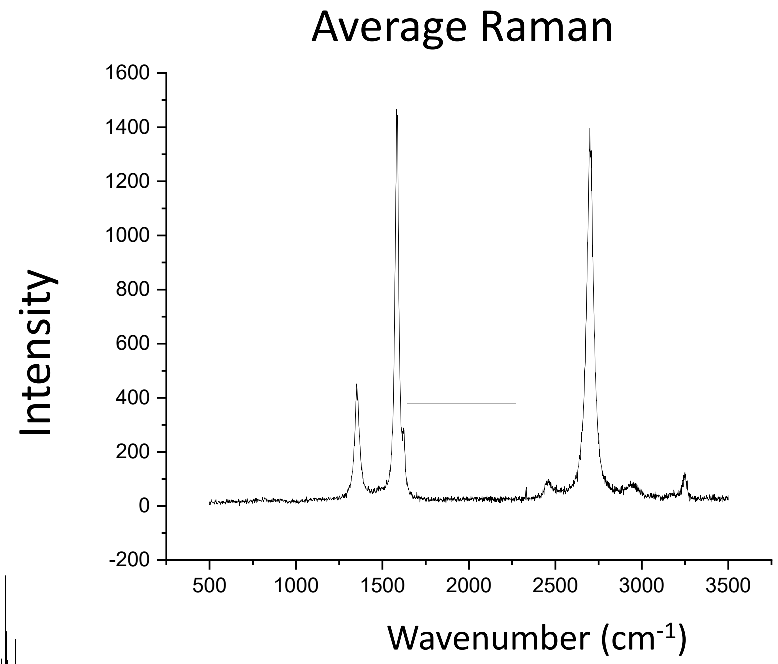
Variable Frequency Drive flashing

- Using variable duty cycle in the same flash, we can further optimize the flash.
- Freestanding flash is demonstrated for the first time with multiple VFD flashing
- Process yield of 40% and 100% graphene yield



Single VFD result in triangle current profile

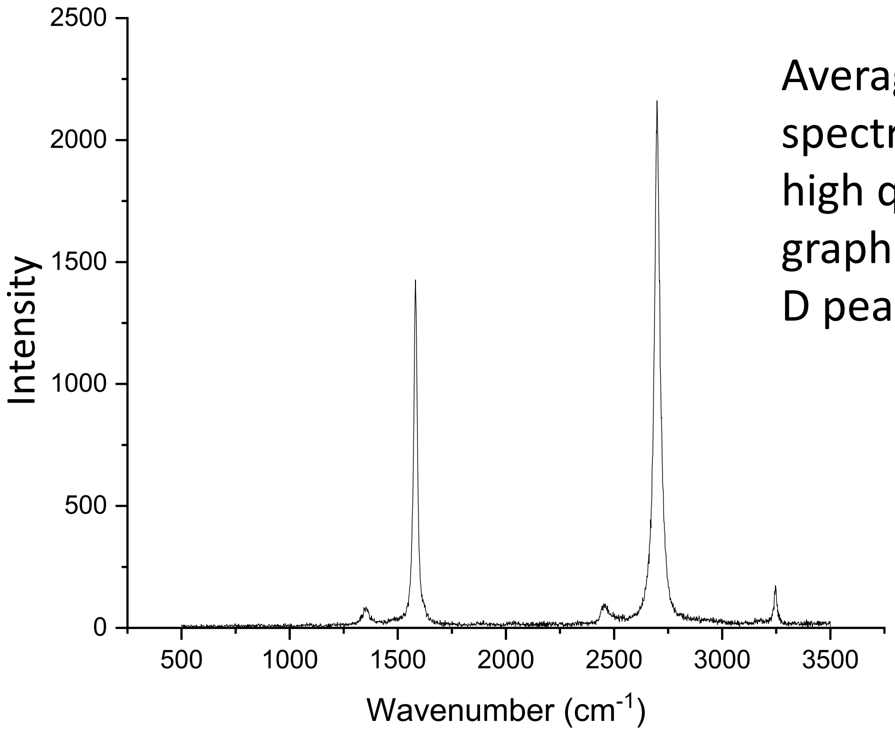




Multiple VFD results in prolonged shape current profile

FJH 5.0 powder flashing

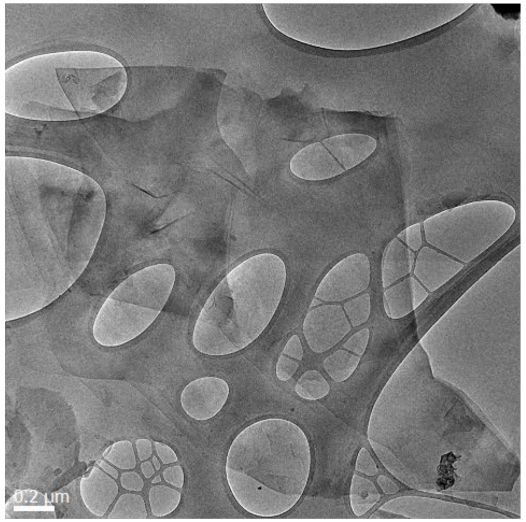
- 5 g batch
- Homogeneous grain size powder provides even flash
- High product yield (flashed material/feedstock) of 90%
- ~100% graphene yield (graphene from flashed material, determined by Raman)
- With VFD flashing, no pretreatment is needed while the graphene yield increases with faster flashing. In 2 h we have made 30 g of flash graphene (0.25 g/min).
- Further manual flashing optimization can result in 1 g/min (1.4 kg/day)

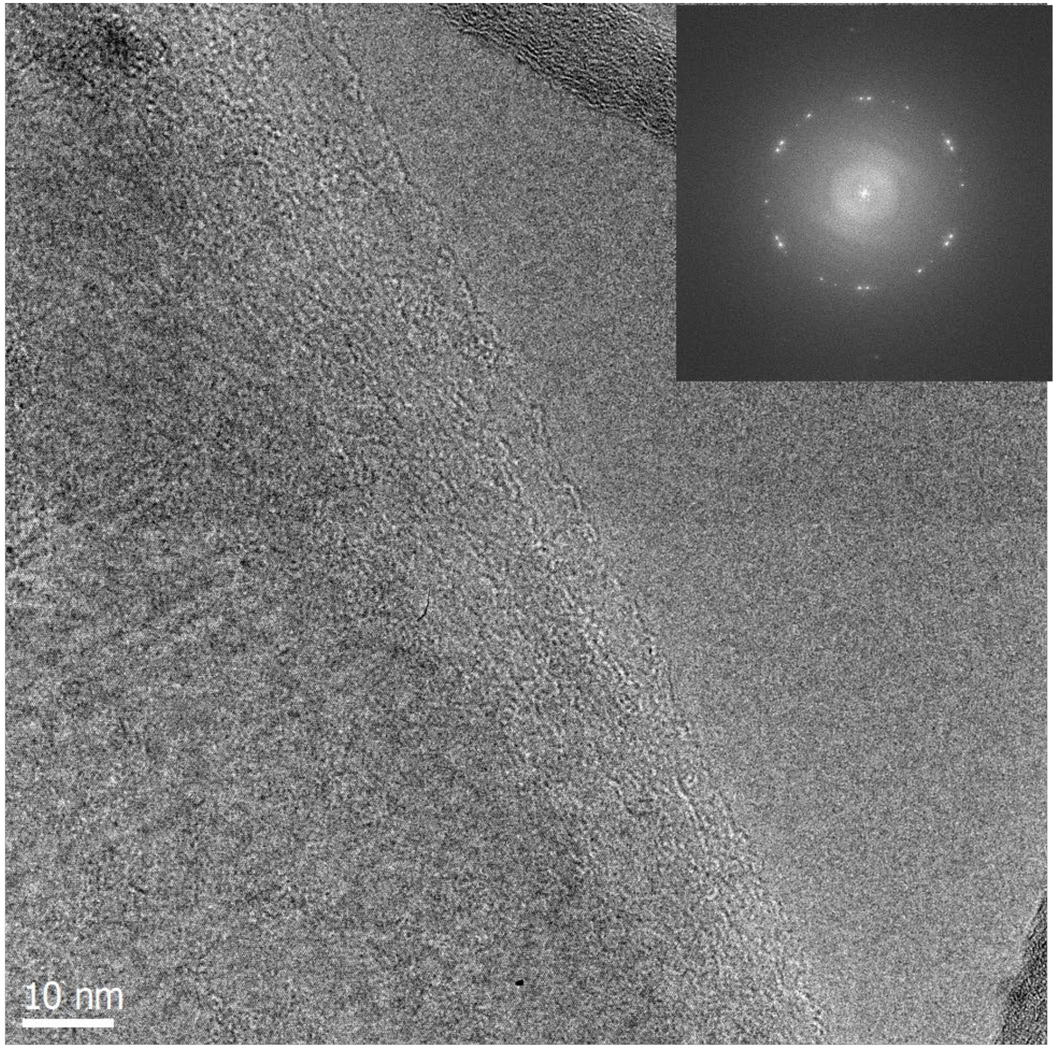


Average Raman spectrum shows high quality of graphene with low D peak and high 2D

FJH 5.0 powder flashing

- 0.2-1 µm in size
- Turbostratic structure seen by HRTEM and FFT.





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 metallurgical coke (MC) per batch to provide > 5.0 g MC flash graphene per batch
- Voltage: 350-400 V, VFD flashing at 1000 Hz, 20% duty cycle
- Process yield: > 90%, graphene yield: ~100%.

VFD PID control

- Multiple VFD for current control
- Control loop base on current and temperature

New Raman system

- Install new Raman system
- Capable of autofocus and mapping
- 121 Raman spectra in 10 min, 10x faster

Worldwide Consumption of Materials per year

	Million tons*	Embodied Energy**
Cement:	4,000	>26B GJ
Concrete:	40,000	
Timber:	3,200	18B GJ
Timber for construction:	< 1,000	
All metals:	1,000	
Steel:	940	
Steel for construction:	< 400	
Paper and cardboard:	300	
Plastics:	120	
Aluminium:	32	

Concrete energy:

- >600 Nuclear Power Plants
- >1800 Hoover Dams

Concrete production produced 5-8% of CO_2 emissions yearly.

https://www.statista.com/statistics/219343/cement-production-worldwide/

Summary

- ✓ Task 3.4: Optimize FJH 5.0 for 10 g flash unit

Due 1 Dec 2020, replaced with VFD flashing of 6 g batches

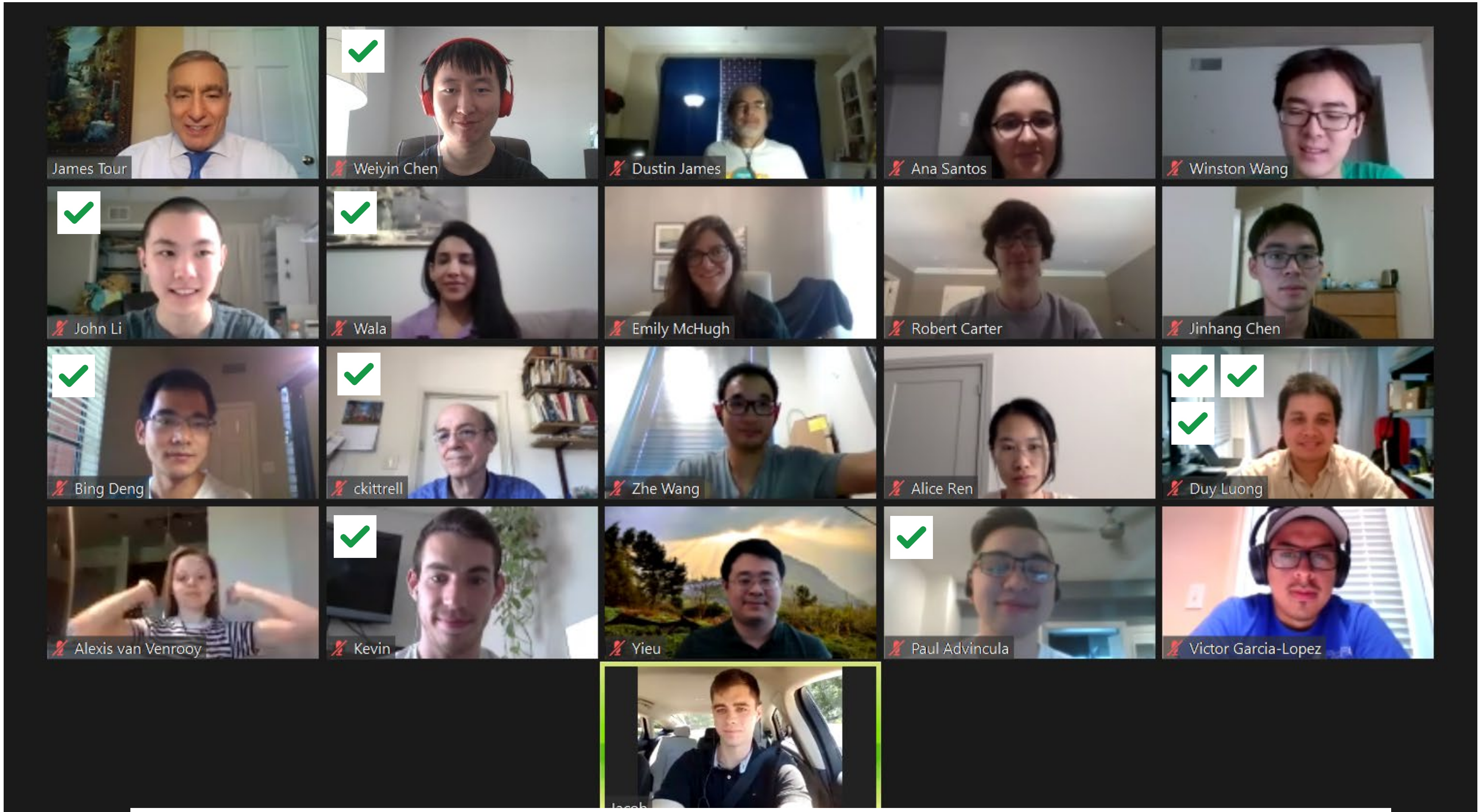
- ✓ Task 3.5: Design of scale-up reactor for 100 g flash

Due 1 March 2021, replaced with automation

- Task 3.6: Build FJH 6.0 for 100 g flash unit

Due 1 June 2021, on schedule

✓ = Flash workers



Thanks to the DOE for support. DE-FE0031794
And Jason Hissam for patience during 2.5 months of lab closure