UNIVERSITY OF DELAWARE
CENTER FOR
COMPOSITE MATERIALS
Celebrating 50 Years

Lab-scale Production of Coal-derived Graphene Particle Bonded Filaments

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Kelvin Fu

Assistant Professor

Center for Composite Materials

University of Delaware

U.S. Department of Energy

National Energy Technology Laboratory

Resource Sustainability Project Review Meeting

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kfu@udel.edu, https://www.kfu-group.com/

Project Overview

- **Funding**

  DOE share: $1,000,000; cost share: $250,000

- **Overall Project Performance Dates**

  February 01, 2022 – January 31, 2025

- **Project Participants**

  Prof. Kelvin Fu, Mechanical, University of Delaware

  Prof. Feng Jiao, Chemical, Washington University in St. Louis

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Project Overview

– **Overall Project Objectives**

The main goal of this project is to develop a lab-scale manufacturing process to fabricate filaments containing coal-derived graphene for 3D printing use.

– To develop filaments for 3D printing that are both carbonizable and highly enriched with coal-derived graphene.
– To develop 3D carbon structures from coal-derived carbon.
– To produce composites reinforced with coal-derived carbon, aiming to achieve mechanical properties suitable for use in structural components.

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Technology Background

- Filament extrusion 3D printing is a cost-effective and popular method for producing plastic components.
- Integrating ceramic and metal particles into the plastic filament, followed by the removal of plastic and sintering, allows for the creation of purely ceramic or metal parts.
- Filaments filled with metal or ceramic materials are already commercially available.
- Filaments designed for 3D printing that can be carbonized have not yet been developed.

Metal-filled filaments

$465, 3kg, 1.75mm, filaments

Coal-filled filaments

Low cost, 1.75mm, filaments

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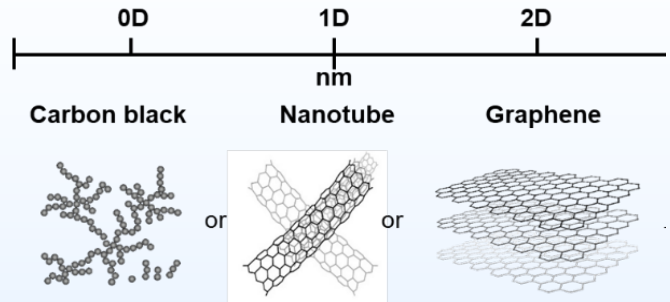
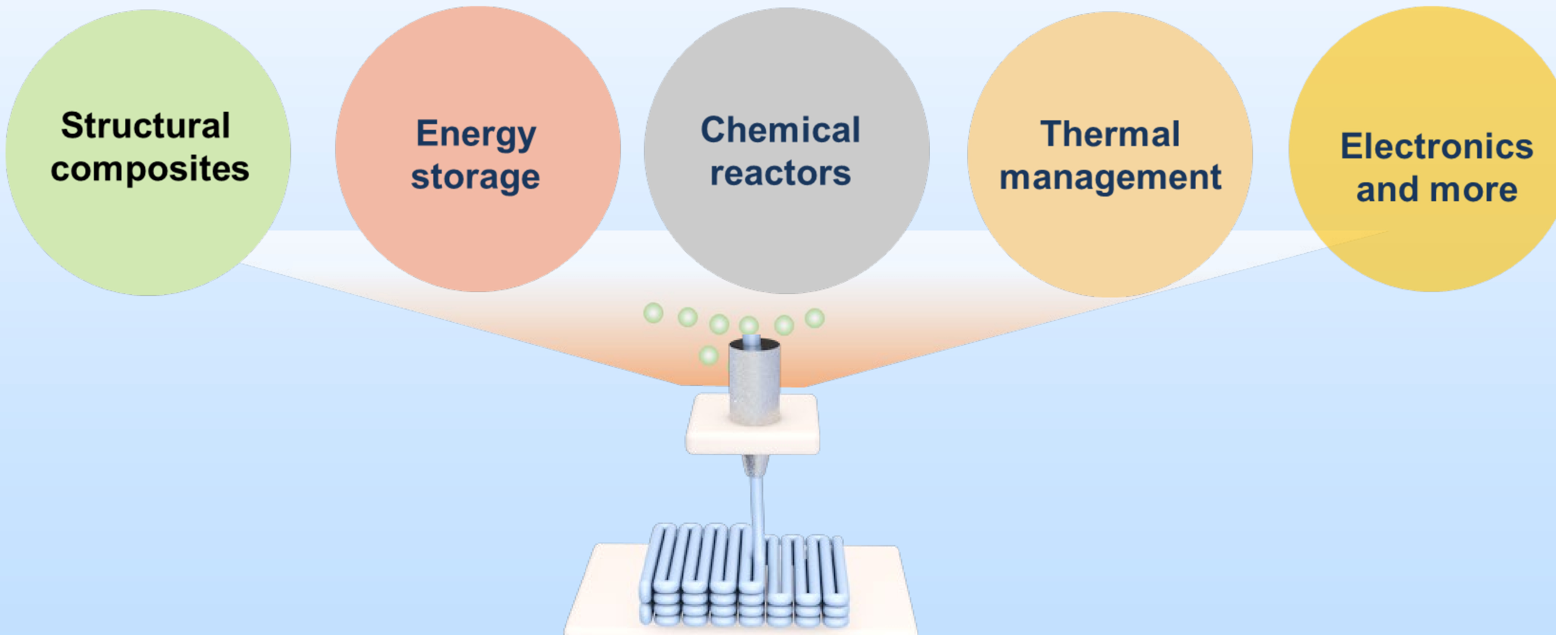
Value-added Coal Applications





Carbonizable filaments, 3D printing, *and* ***post processing***

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Technical Approach/Project Scope

a. Project steps and work plan

Particle Bonded Filament Technology

Coal-derived carbon treatment and polymer crafting

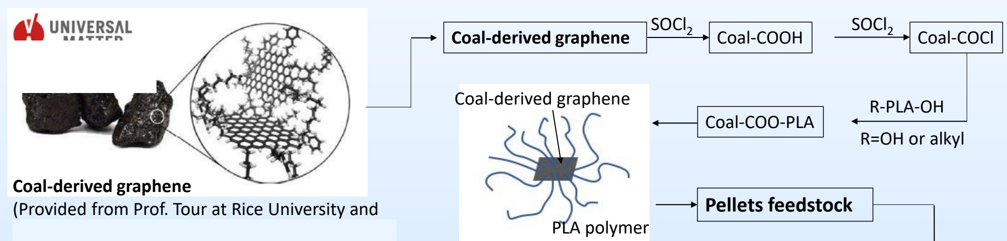
Phase I

Filament production (target loading 50 wt. %)

Phase I

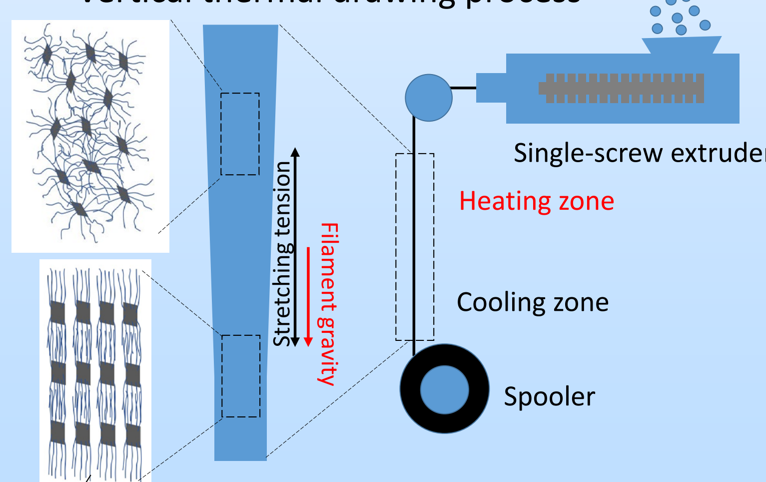
Contaminates examining and treatment

Polymer grafted coal-derived graphene hybrid



Vertical thermal drawing process

- Polymer chains flow and orient along with shear flow-induced coal-derived graphene alignment in heating zone
- Aligned and densely packed polymer chain and coal-derived graphene can be freezed in cooling zone.



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Technical Approach/Project Scope

a. Project steps and work plan

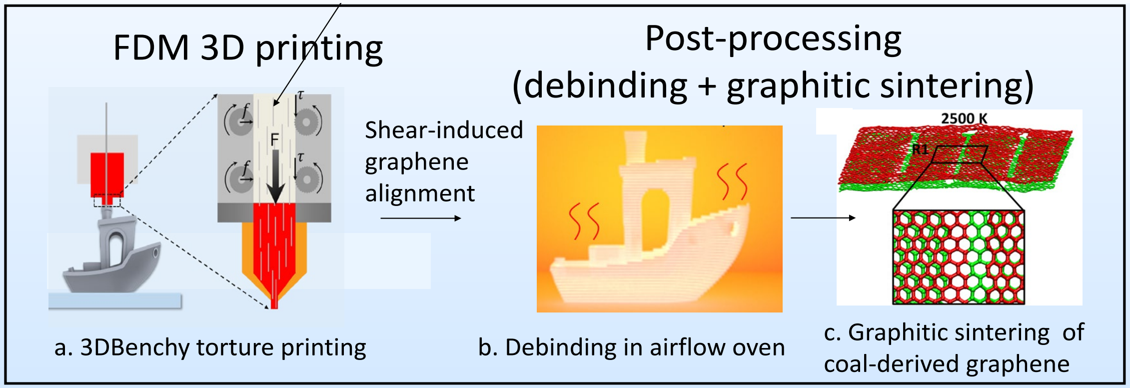
FDM 3D printing, debinding and sintering to fabricate fully carbon preform

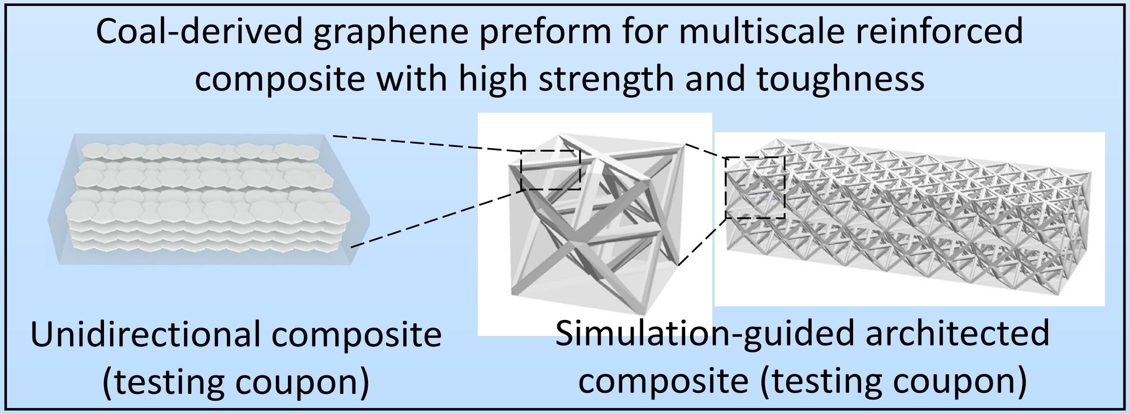
Phase II

Coal-derived graphene preform reinforced polymer composite

Phase II

Techno-economic assessment





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Technical Approach/Project Scope

b. Key milestones

- Develop filaments containing carbon loadings of 20 and 50 weight percent (wt.%).
- Utilize an FDM (Fused Deposition Modeling) 3D printer to produce objects using the developed filament.
- Fabricate carbon reinforcement through 3D printing and carbonization.
- Manufacture coal carbon reinforced composites (tensile strength 800 MPa).

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Technical Approach/Project Scope

c. Project risks and mitigation strategies

Risk:

- Filaments (diameter 1.75 mm; carbon loading >30 wt.%) cannot be created using the traditional horizontal drawing method.

Mitigation strategy:

- Utilize a vertical drawing method to fabricate the filaments.

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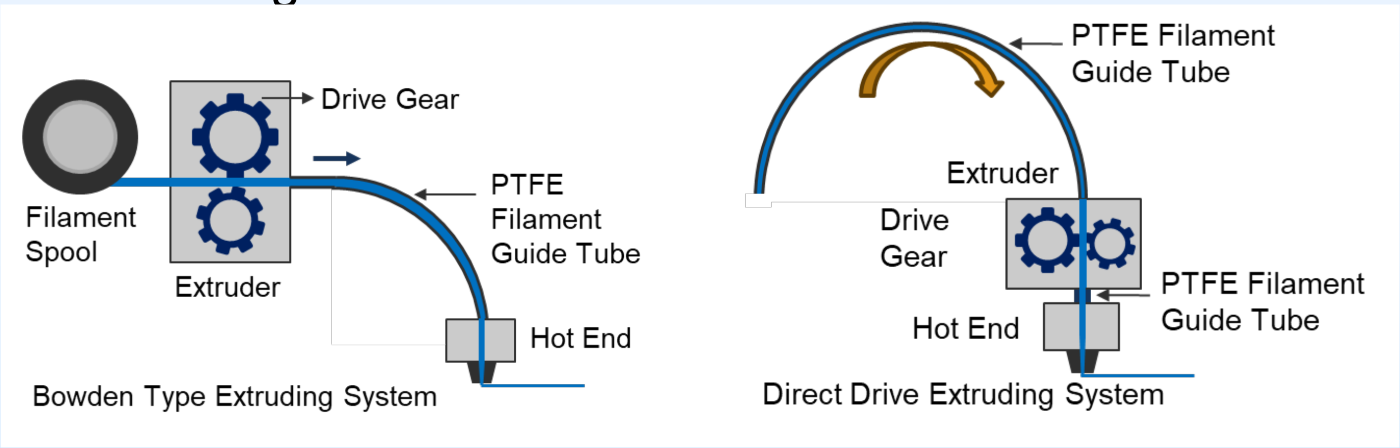
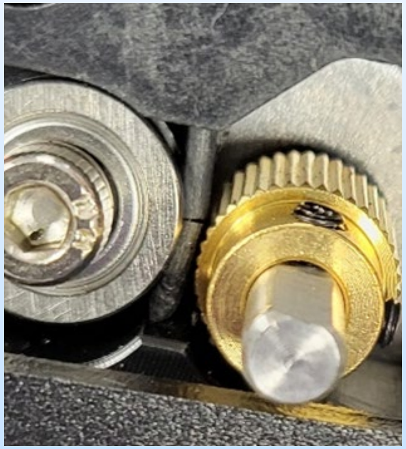
Technical Approach/Project Scope

c. Project risks and mitigation strategies

Risk:

- The extruder head of a FDM printer is not capable of printing filaments with a high carbon content.





Mitigation strategy:

- Design and develop a specialized extruder head tailored for 3D printing with filaments that have a high carbon load.

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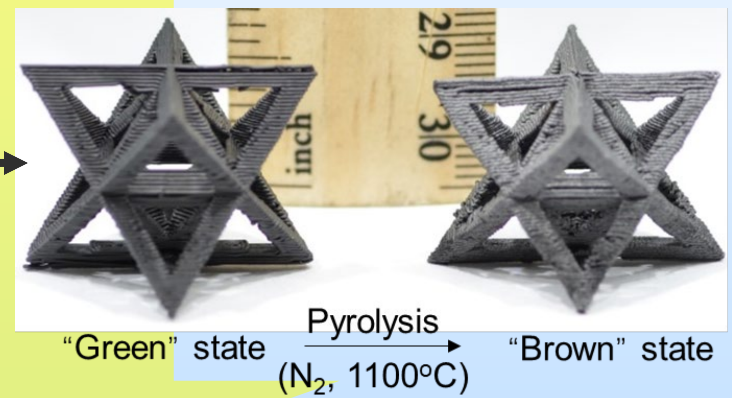
Challenges

Coal-derived carbon

* Filament production   * 3D printing   * Polymer removal



Carbon reinforced thermoset composites

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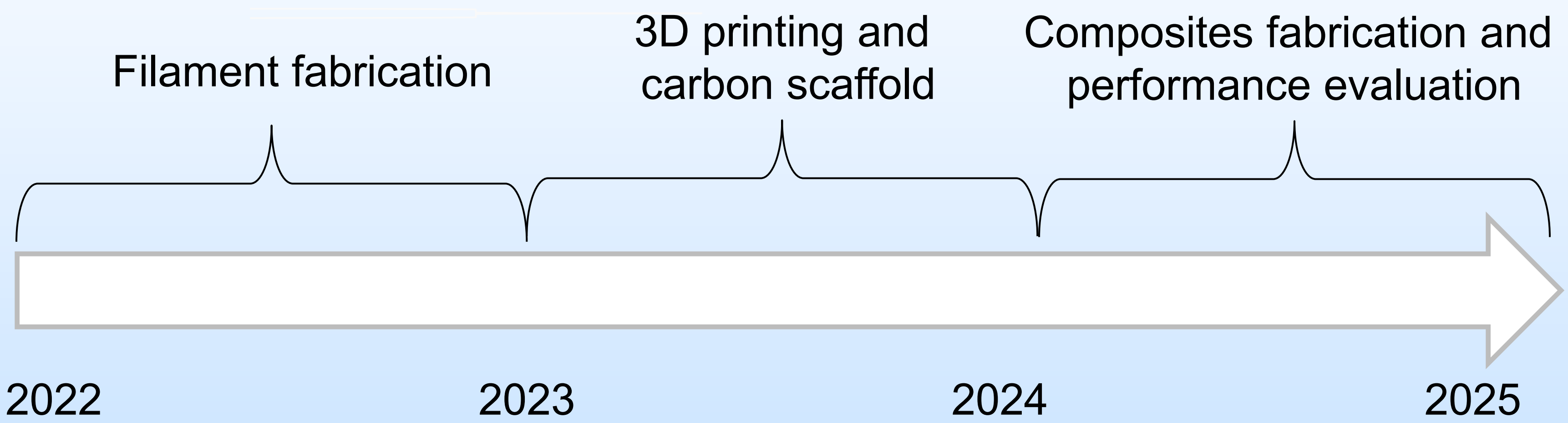
Project Schedule



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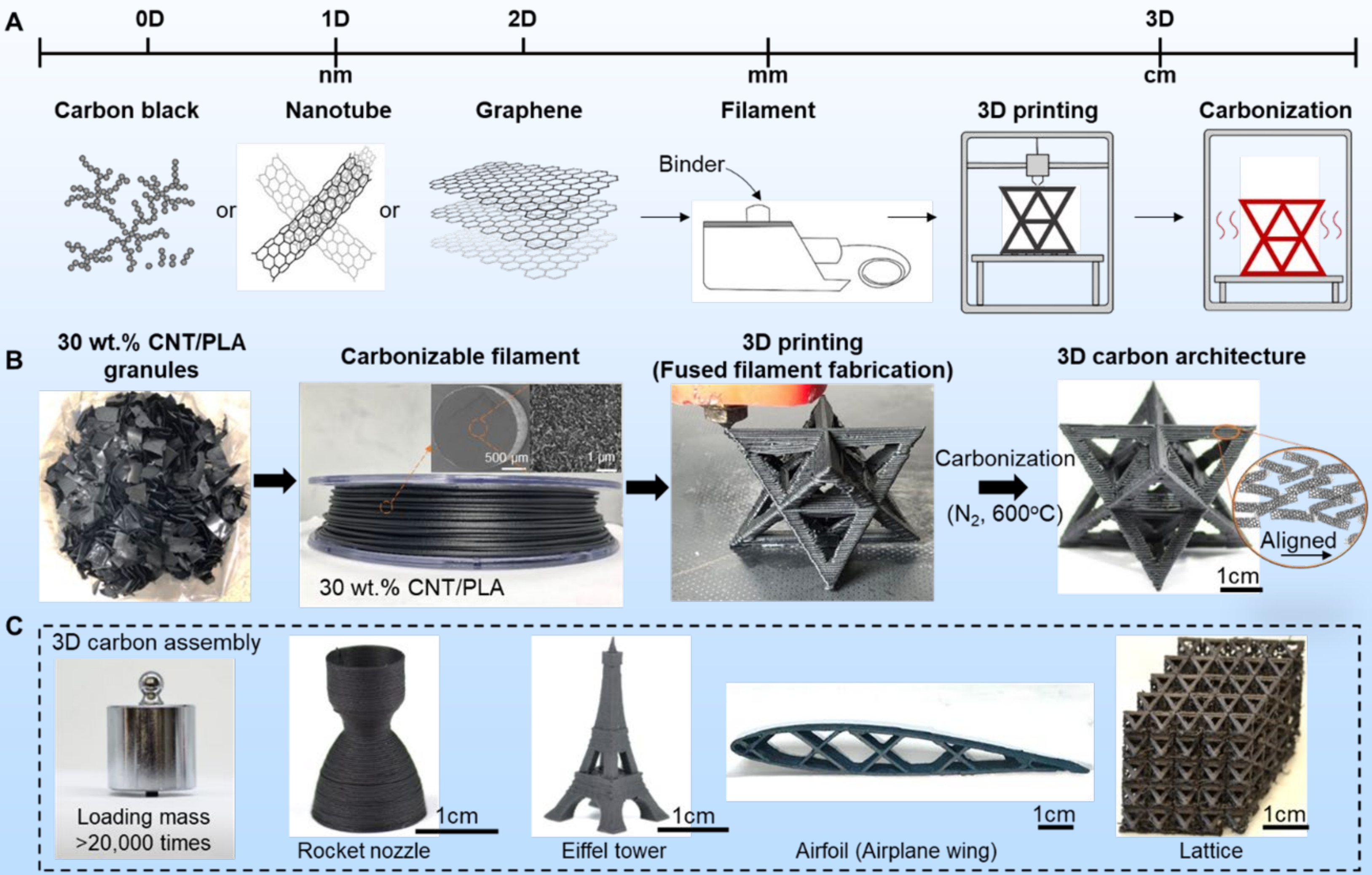
Progress and Current Status of Project



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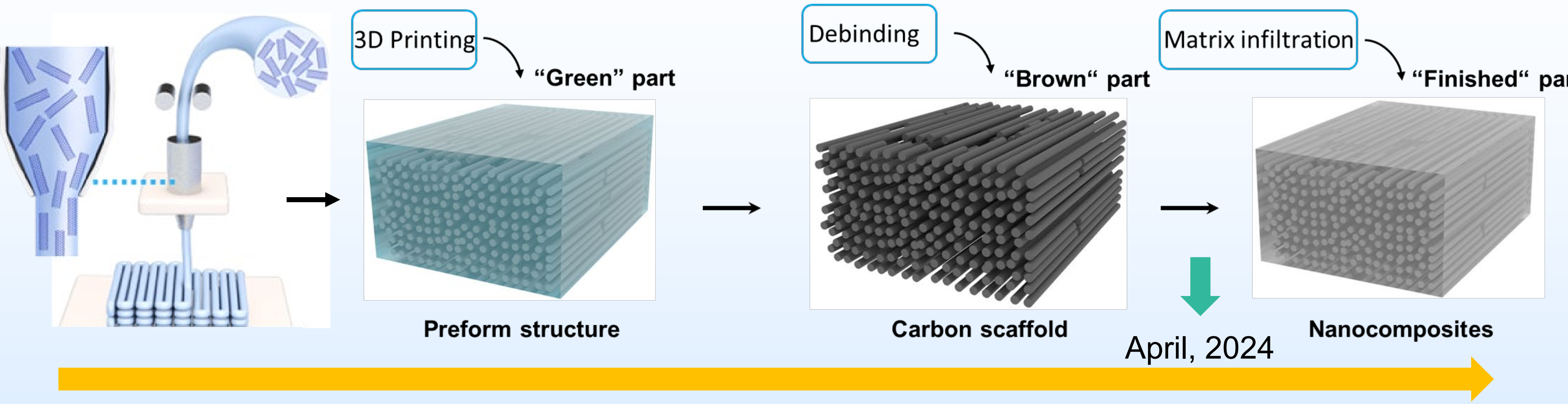
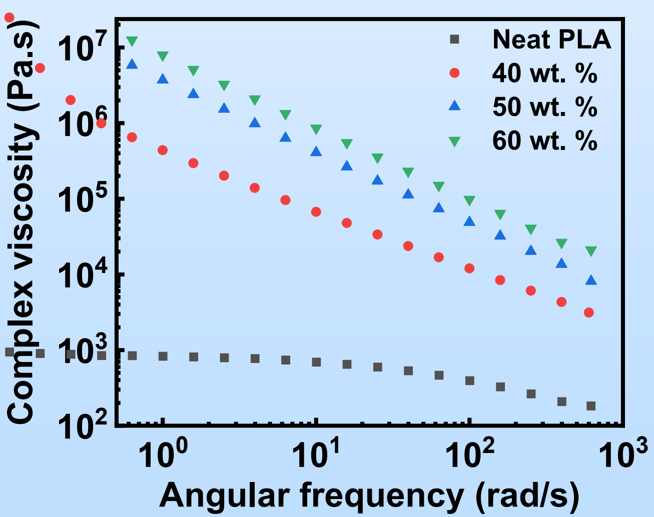
“Green-to-Brown” States Transition





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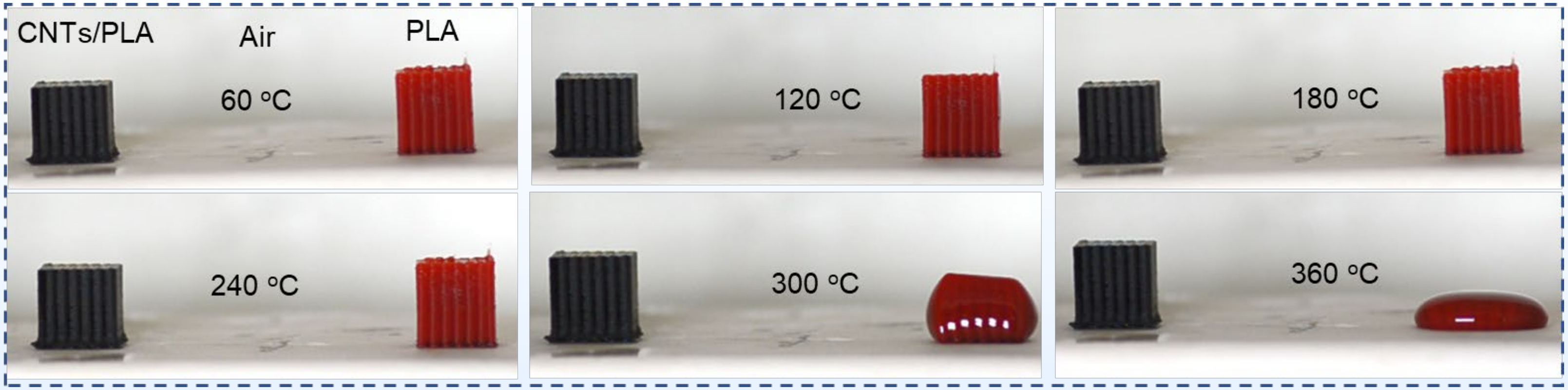
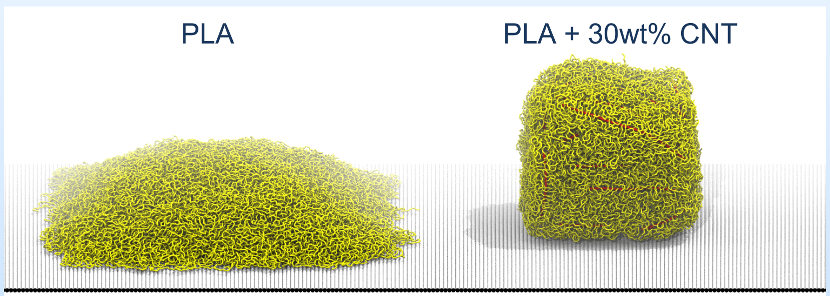
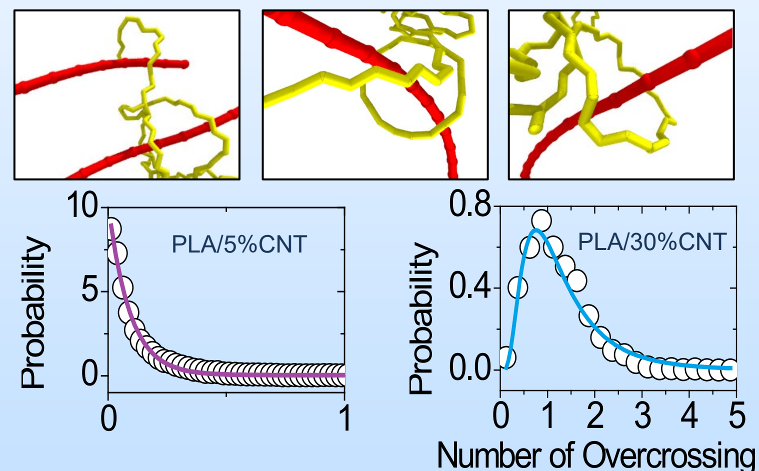
Molecular Origins of Enhanced Thermal Stability

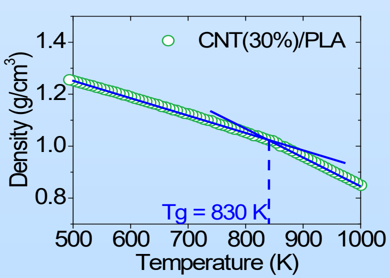




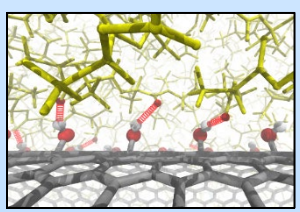
- PLA/30wt%CNT retains shape at 600 K

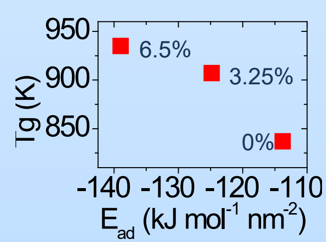


- Molecular origin: overcrossing (entanglement) is enabled by adding sufficient CNT



- Adding 30wt% CNT improves the glass transition temperature from 346 K to 830 K





- H bonds improves T_g

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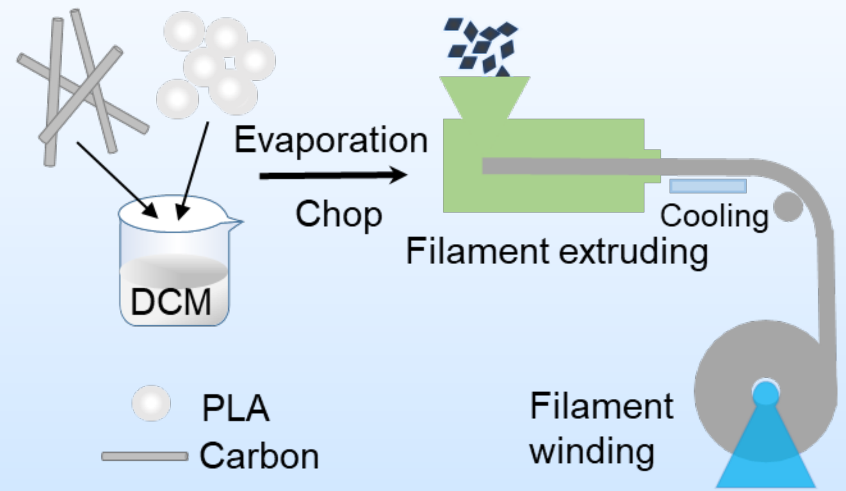
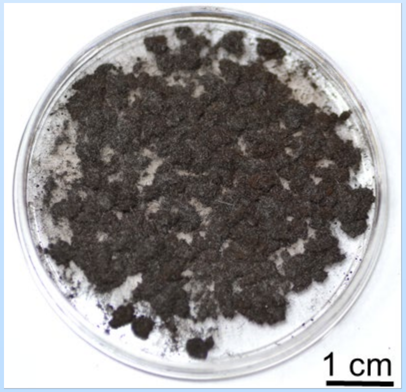
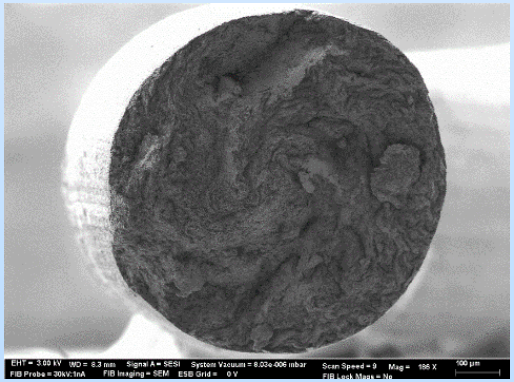
Filament Fabrication

- The vertical drawing method addresses the issues of sagging and low stretchability of filaments with high carbon content encountered in the horizontal drawing process.







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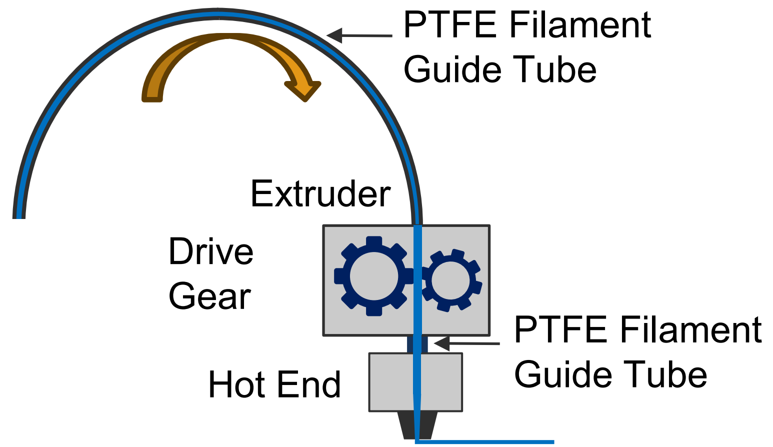
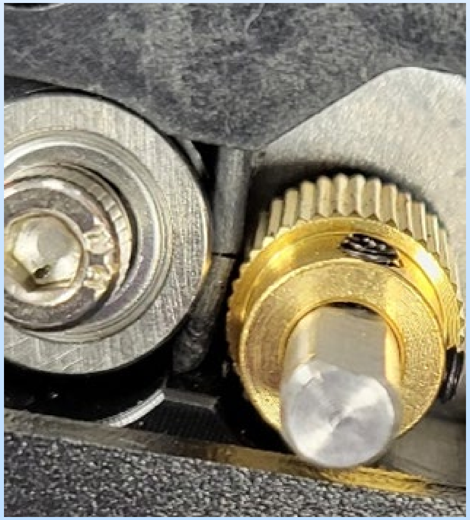
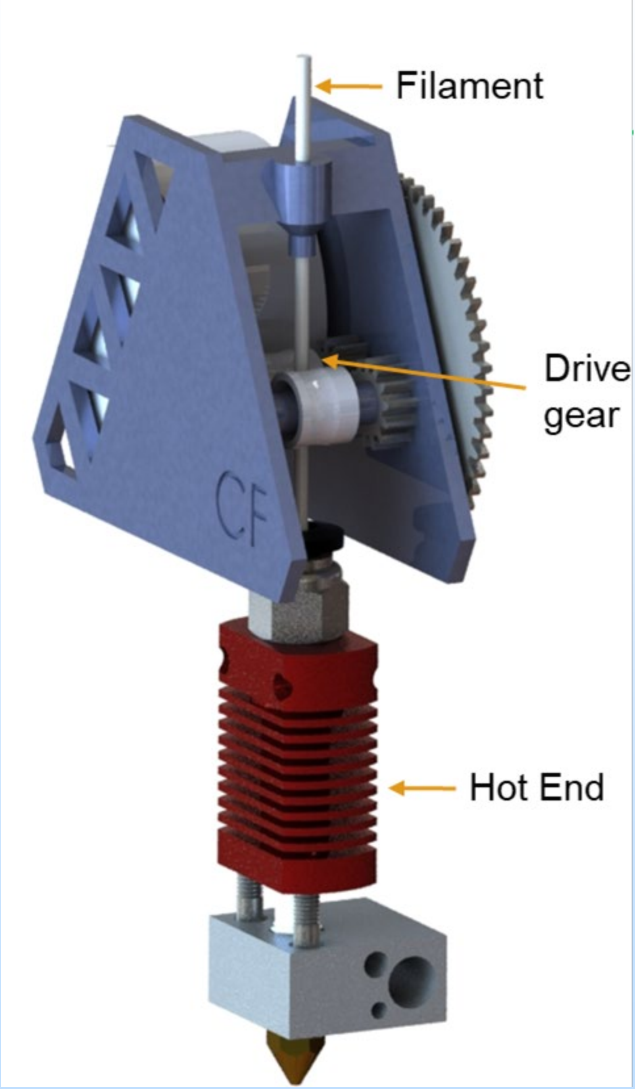
3D Printing and Extruder Design



Direct Drive Extruding System





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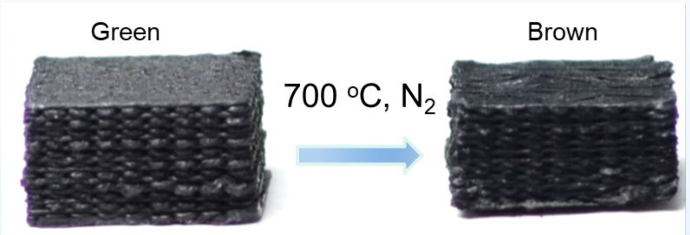
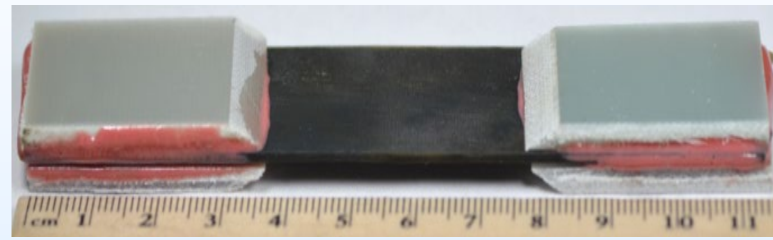
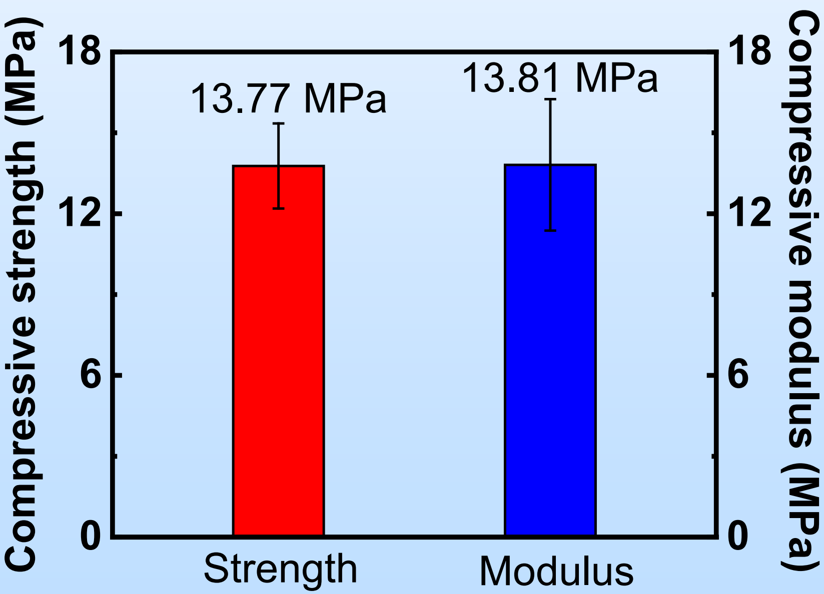
Carbon scaffold and composites fabrication

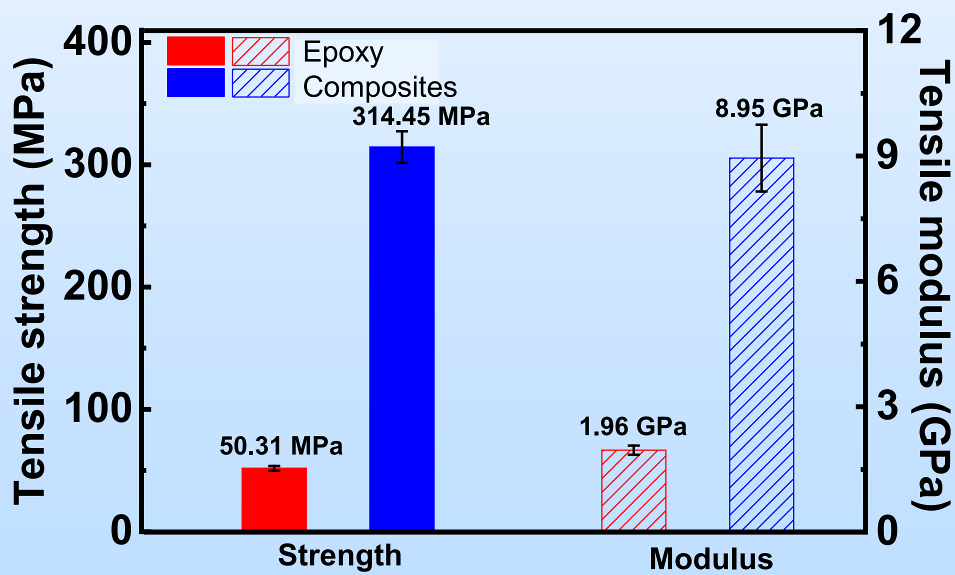
3D printing Carbonization



Vacuum-assisted epoxy infiltration and curing







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Plans for future testing/development

In this project, our ongoing efforts include:

1. **Enhancing the bonding strength** of coal-derived carbon particles to improve structural integrity.
2. **Increasing the density** of the carbon scaffold to achieve greater material robustness.
3. **Improving the printability** of high carbon-loaded filaments by refining the extruder head design, adapting it for more effective processing of these materials.
4. **Elevating the carbon volume fraction** in composites, aiming for superior performance characteristics.

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Plans for commercialization

Our commercialization strategy post-project includes the following key initiatives:

1. **Diversifying our range of coal-derived carbons** to encompass various forms such as powders, carbon nanotubes (CNTs), graphene, and fibers. This expansion aims to produce a versatile array of carbonizable filaments tailored for 3D printing applications.
2. **Launching a specialized extruder head**, uniquely engineered for the efficient 3D printing of high carbon-loaded filaments, thereby meeting a specific market need.
3. **Developing a complete 3D printer system**, which includes our specially designed extruder head and a heating enclosure. This system is engineered to minimize part delamination during printing, offering a robust solution for high carbon filament printing.

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Summary

- We can now produce **carbonizable filaments** with up to 50 wt.% carbon loading
- The **vertical drawing method** for filament fabrication shows better results compared to the horizontal approach.
- Our **redesigned extruder head** has improved the printing process, reducing issues like nozzle clogging and filament breakage.
- Using **hot isostatic pressure** during carbonization could help in minimizing delamination of samples.

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Acknowledgement

- Team members
- Program manager: Sandy J Napolitano

Thank you!

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Appendix

- These slides will not be discussed during the presentation but are mandatory.

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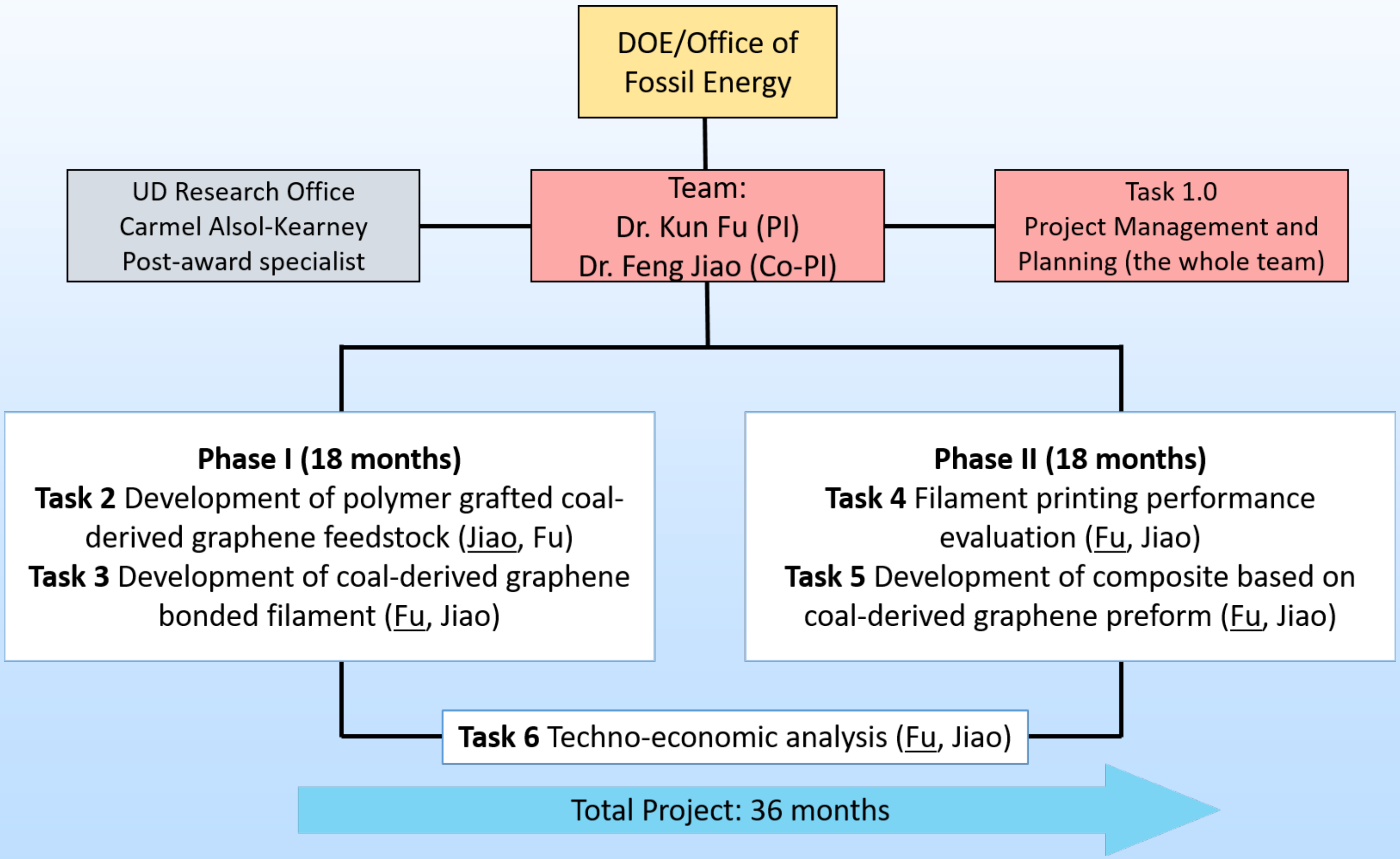
Organization Chart



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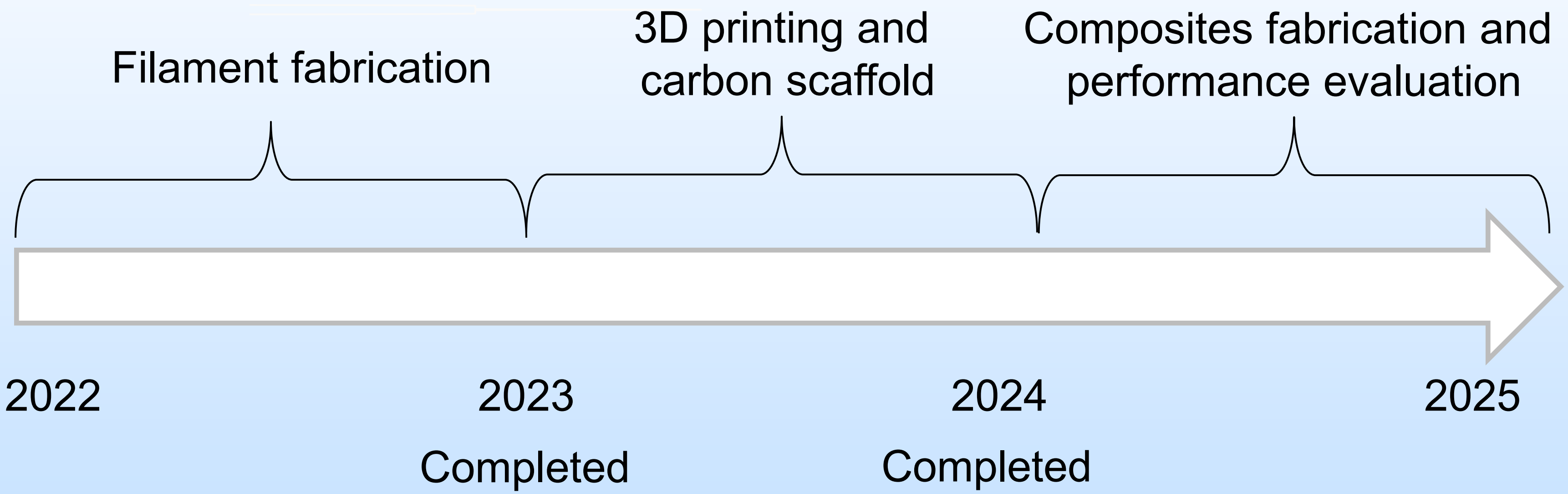
Gantt Chart


Filament fabrication
3D printing and carbon scaffold
Composites fabrication and performance evaluation
2022
2023
Completed
2024
Completed
2025