UNIVERSITY OF DELAWARE
CENTER FOR
COMPOSITE MATERIALS
Celebrating 50 Years

Lab-scale Additive Manufacturing of Coal-derived Carbon-Metal Composites for High-Performance Heat Sinks FE0032280

PI: Kelvin Fu, University of Delaware

Co-PI: Zhe Qiang, University of Southern Mississippi

04/04/2024

Project Overview

– **Funding**

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

– **Overall Project Performance Dates**

September, 2023 – August, 2025

– **Project Participants**

Prof. Kelvin Fu, Mechanical Engineering, University of Delaware

Prof. Zhe Qiang, Polymer Science and Engineering, University of Southern Mississippi

Project Overview

- **Goal:** To develop a lab-scale additive manufacturing (AM) process to fabricate carbon-copper composites with a high heat dissipation rate and low thermal stress and demonstrate highly-efficient and compact heat sinks for electrical applications.

- Specific objectives include:

1. To develop a new feedstock containing coal-derived graphene and high-carbon-yielding polymers for extrusion 3D printing;
2. To develop an extrusion 3D printing and sintering process to fabricate strong carbon and copper structures;
3. To develop coal-derived graphene-copper composites with high heat dissipation rate and low thermal stress.

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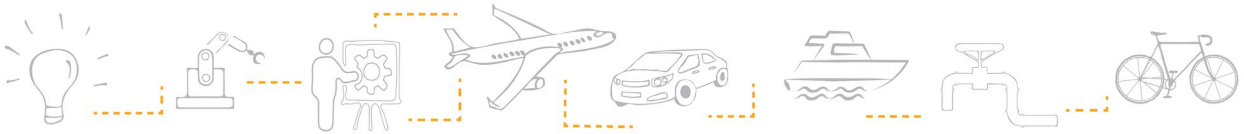

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Key Expected Outcome/Milestones

- **Phase I (Budget Period 1, 12 months):** development of an **additively manufactured coal-derived graphene-metal composites** in the form of a flat coupon, with aim to meet the following criteria: **< 20 vol.% shrinkage** of graphene-polymer after graphitization, graphene loading of up to **30 wt. % in the composite**, graphene alignment to the printing path of up to 50%, graphene preform structure compressive strength of up to or in excess of **60 MPa**, graphene-copper in-plane **thermal conductivity reaching 400 W/mK**, graphene-copper through-plane coefficient of thermal expansion **(CTE) reaching 10×10^{-6}/K** with high stability after repeated thermal fatigue tests between 25°C and 150°C (approximately 500 cycles).

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Key Expected Outcome

- **Phase II (Budget Period 1, 12 months):** development of **additively manufactured graphene-copper heat sinks**, with aim to meet the following criteria: **< 5 vol.% shrinkage** of graphene-polymer after graphitization, graphene loading of up to **50 wt. %** in the composite, graphene alignment relative to the printing path up to 80%, graphene preform structure compressive strength of up to or in excess of **100 MPa**, graphene-copper in-plane **thermal conductivity reaching 450 W/mK**, graphene-copper through-plane **CTE reaching 5×10^{-6}/K**, with high stability after repeated thermal fatigue tests between 25°C and 150°C (approximately 1000 cycles).

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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.
- Adding metal particles into carbonizable filaments could enhance conductivity and mechanical performance.
- Expanding the range of applications for coal-derived carbon to include high-value products.

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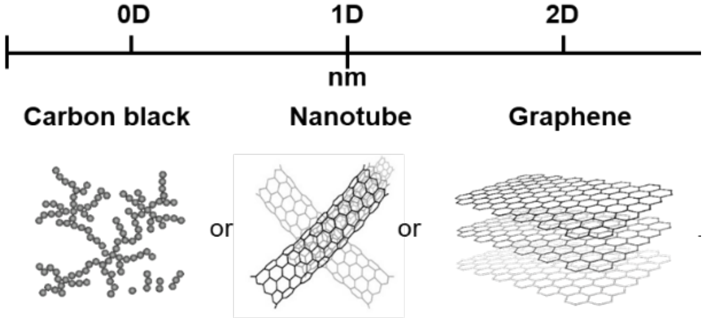
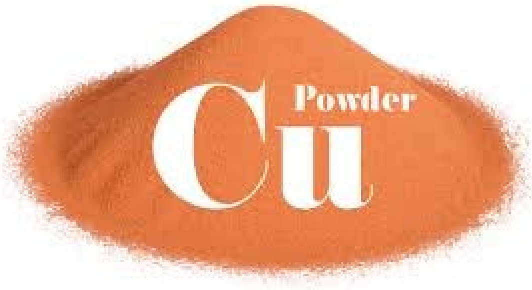
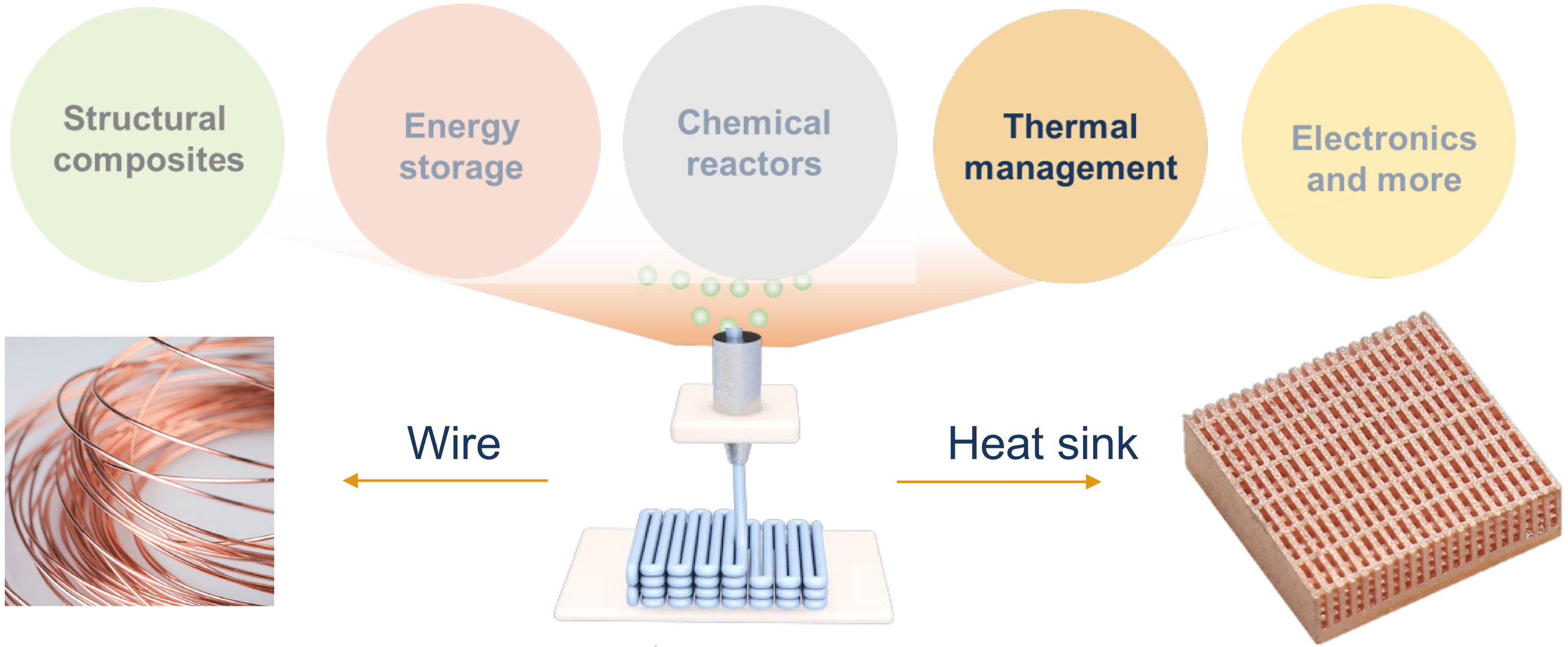
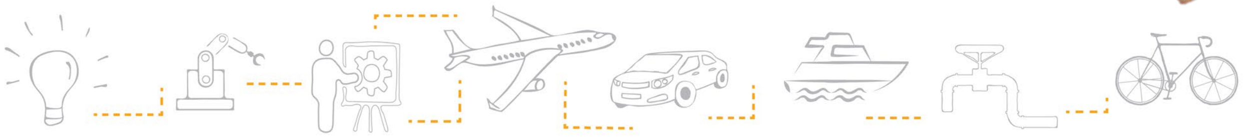
Adding Value to Coal Applications









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Technical Approach/Project Scope

Coal carbon (graphene)

High carbon-yield polymer

Copper nanopowders

→ Pellets and 3D printable filaments → FDM 3D printing and sintering

(To enable graphene alignment for improved thermal and mechanical property)

→ Second copper infiltration

→ Thermal property characterization

→ Heat sink design and fabrication

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Technical Approach/Project Scope

Graphene –polymer AM feedstock development

↓

Additive manufacturing of graphene-polymer "green" part

↓

Graphene preform structure

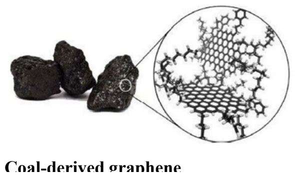
↓

Wettability and interfacial bonding improvement between graphene and copper

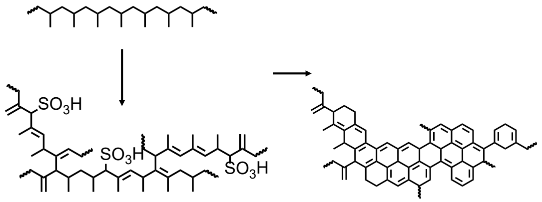
↓

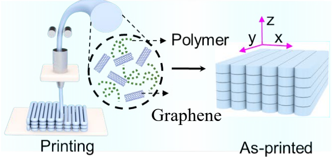
Graphene preform impregnation with molten copper & graphene-copper composite heat sink demonstration

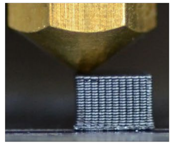
Contaminates examining and treatment

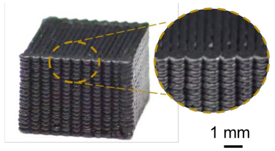


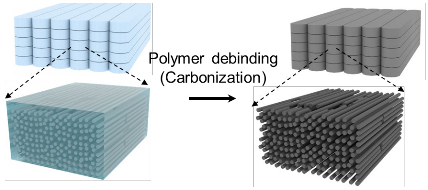
High-carbon-yielding polymer functions as binder











Formation of graphene prefo

Approach 1:

- Add alloying element (Ti, Cr, Si) to copper to form an alloy.
- In the infiltration process, alloying element diffusion in copper matrix and formation of carbide at the copper-carbon interphase.

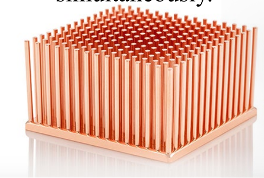
Approach 2:

- Chemical Vapor Deposition (CVD) or electrodeposition of alloying element onto graphene preform structure.
- During molten copper infiltration, alloying and carbide formation will occur simultaneously.

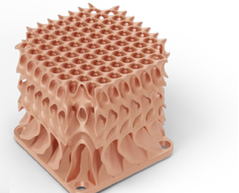
Gas pressurized infiltration method

→

to infiltrate molten copper into graphene preform



Fin-based



Lattice-based

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Technical Approach/Project Scope

Risk:

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

Mitigation strategy:

- Utilize a vertical drawing method to fabricate the filaments.

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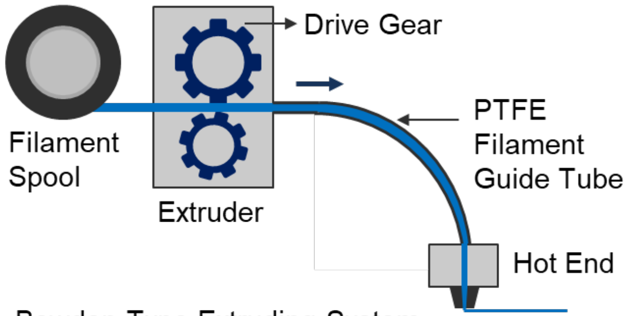
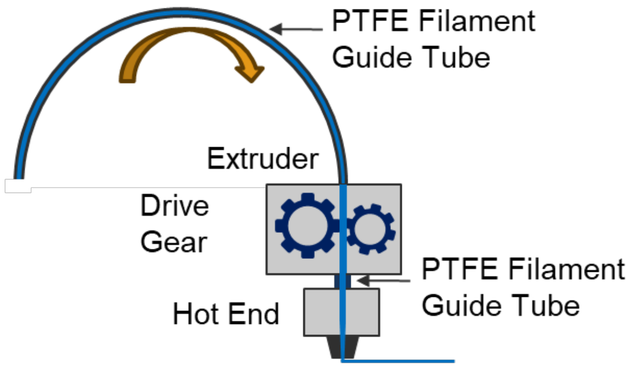
Technical Approach/Project Scope

Risk:

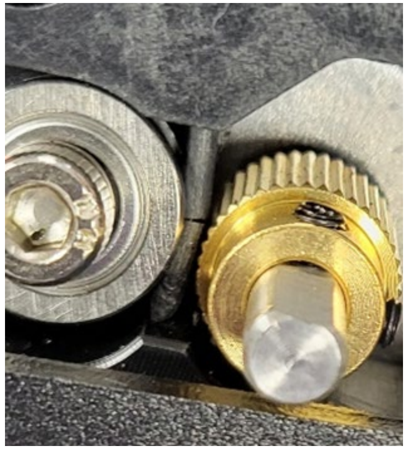
- The extruder head of a FDM printer is not capable of printing filaments with a high carbon content.



Bowden Type Extruding System



Direct Drive Extruding System



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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Technical Approach/Project Scope

Risk:

- The low mechanical bonding strength of coal carbon particles limits their thermal conductivity, presenting a challenge for applications where high heat transfer is required.

Mitigation strategy:

- Utilize polyacrylonitrile (PAN) polymer to create a graphitic carbon layer, which will effectively bond coal particles within the carbon scaffold.

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Challenges

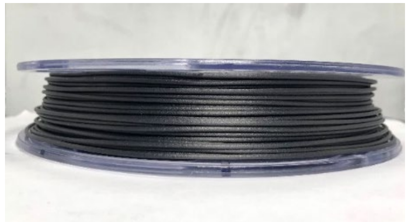
Coal-derived carbon + copper

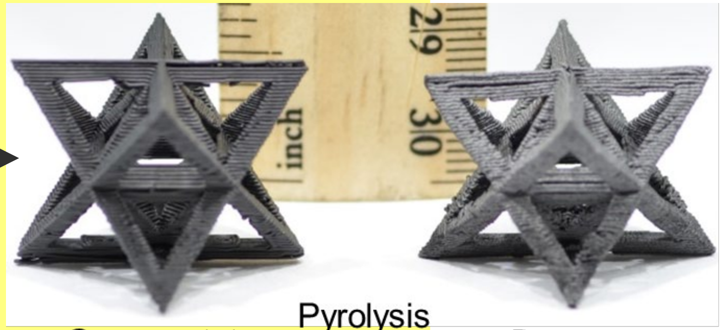
* Filament production

* 3D printing

* Carbon yielding

* Copper bonding



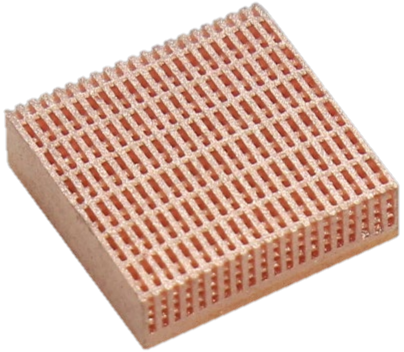


"Green" state

Pyrolysis

(N_2, 1100°C)

"Brown" state



Highly thermal conductive coal-copper composites

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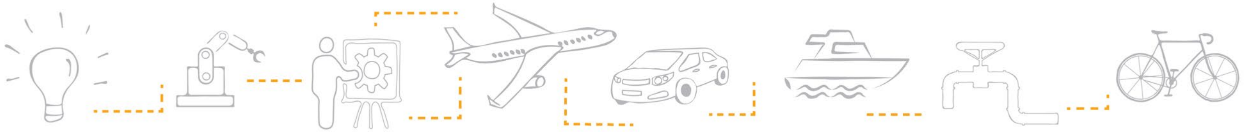

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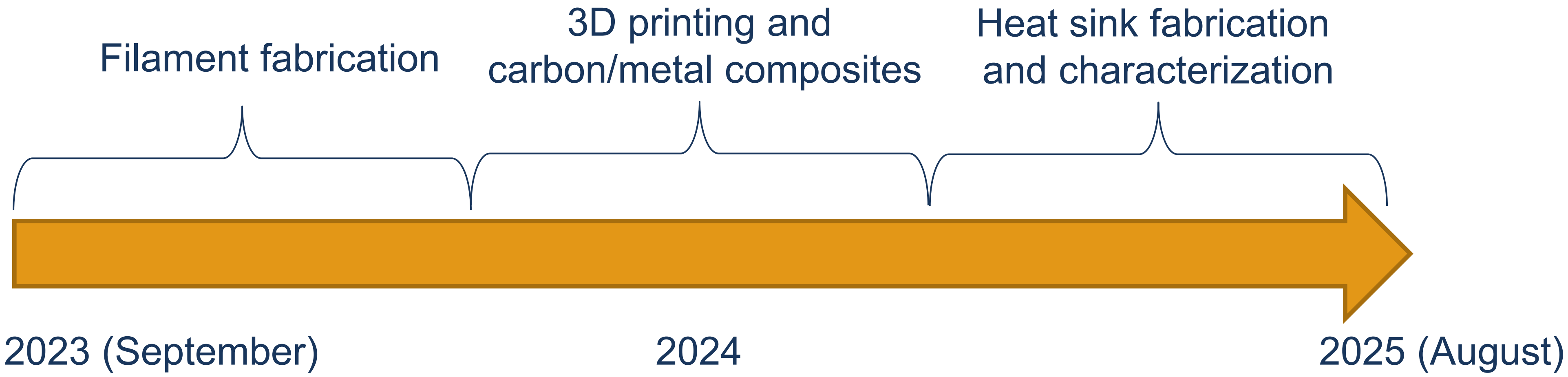
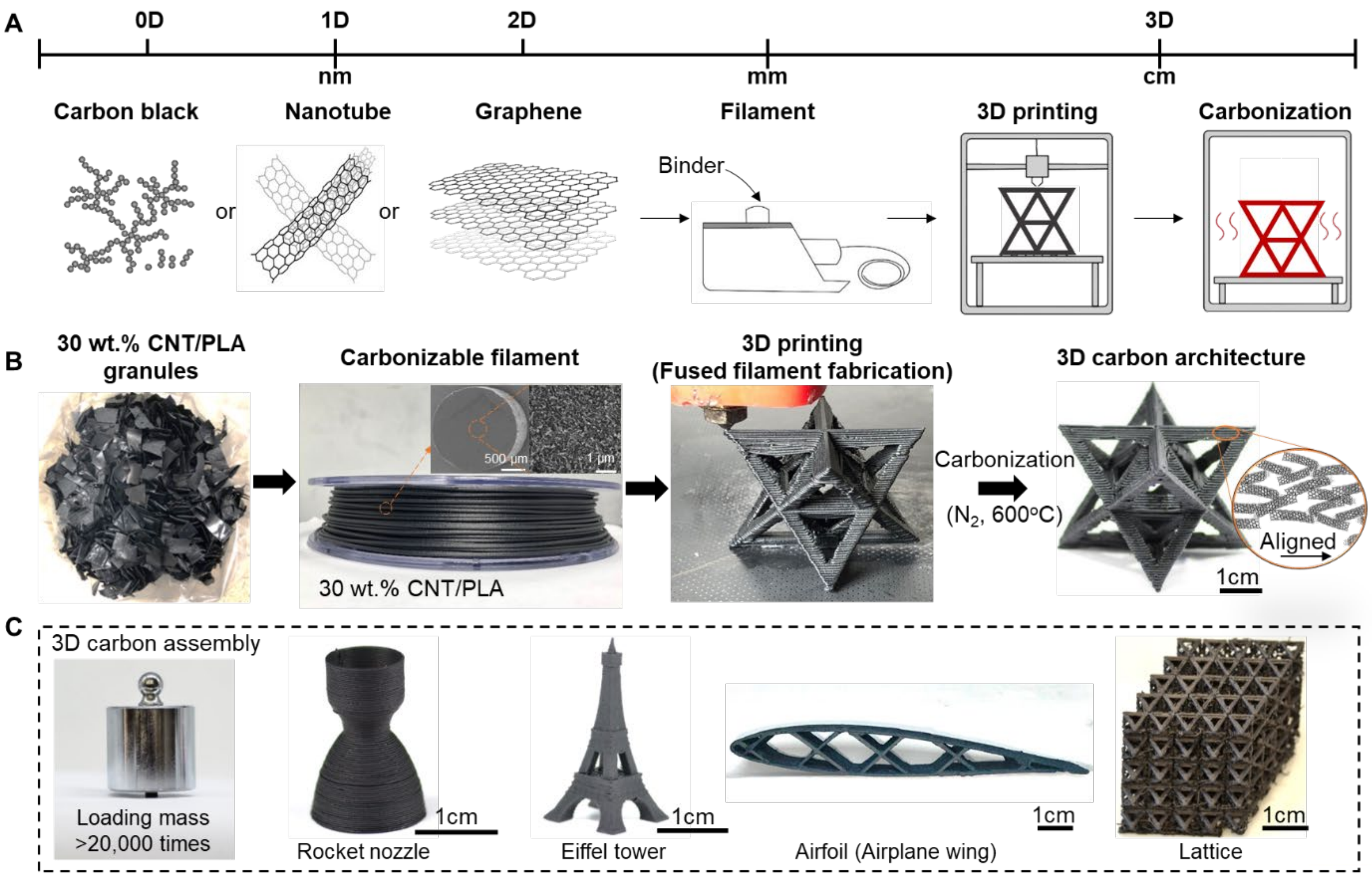
Project Schedule



Coal-enhanced PP filament (completed)

Coal/copper-enhanced PP filament (ongoing)

Progress and Current Status of Project



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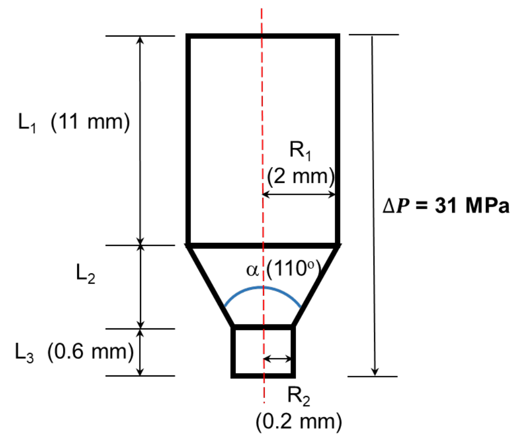
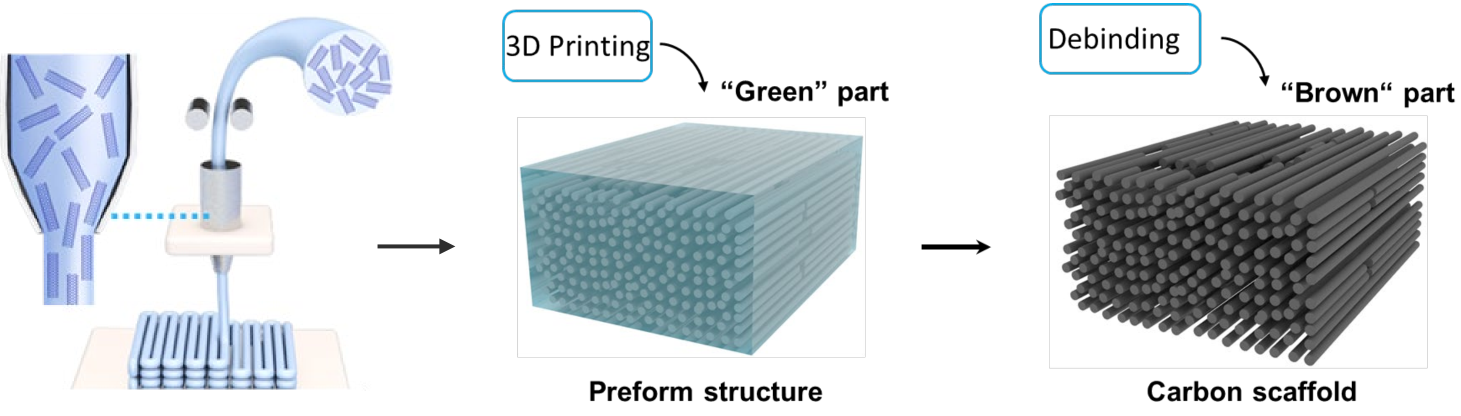
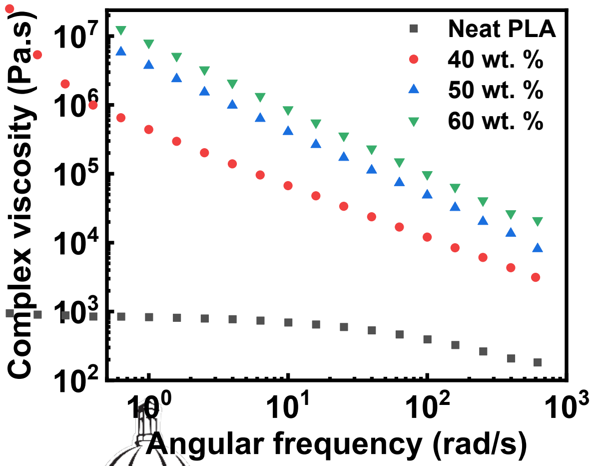
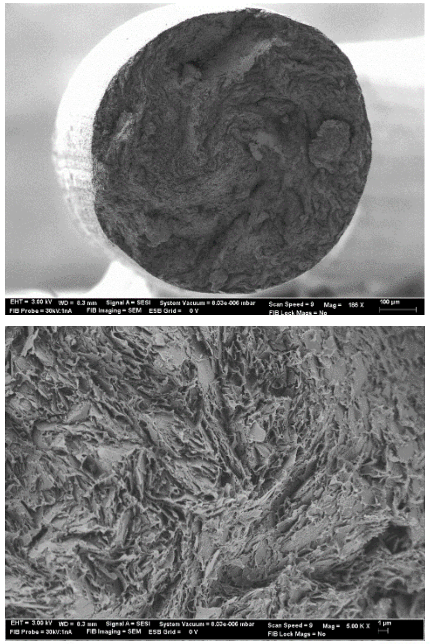
Shear Assisted Particle Extrusion (SHAPE) and "Green-to-Brown" Transition Strategy









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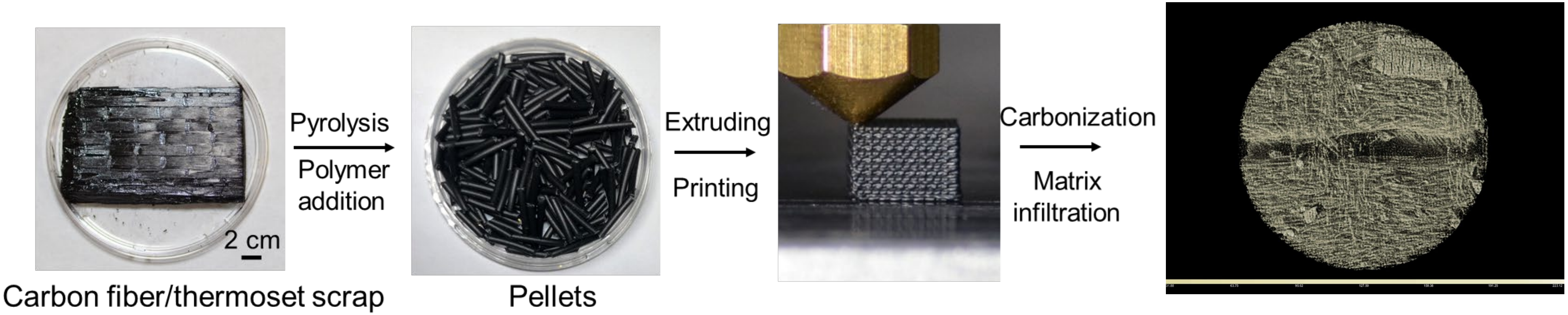
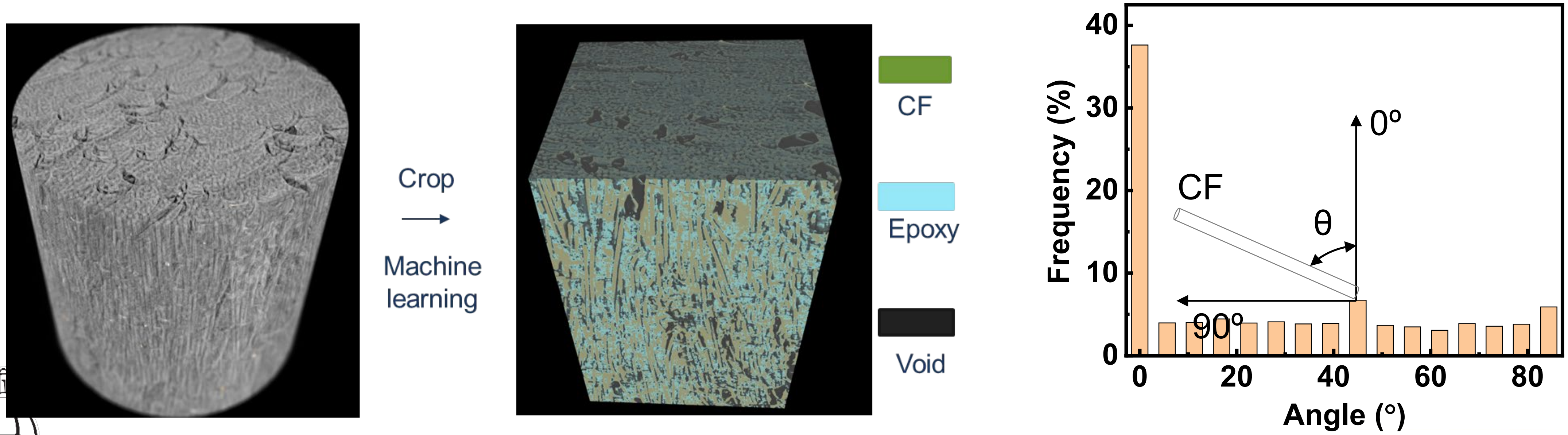
Realigning Short Carbon Fiber by Shear Force





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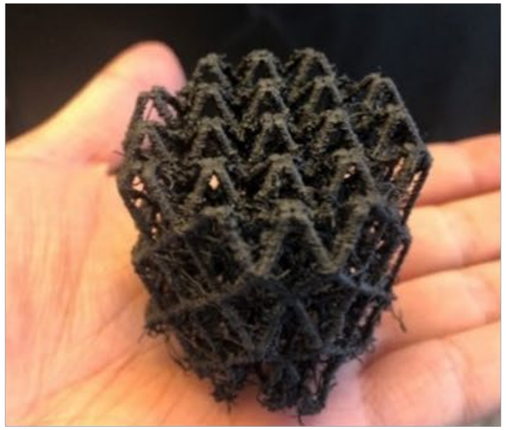
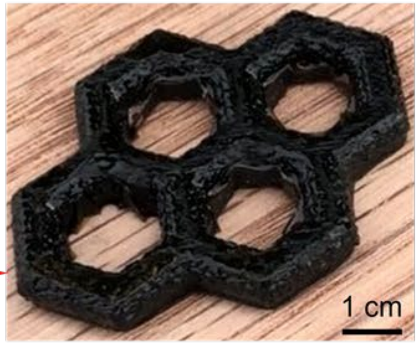
Carbon Scaffold for Composites

Scaffold

Impregnating matrix ↓

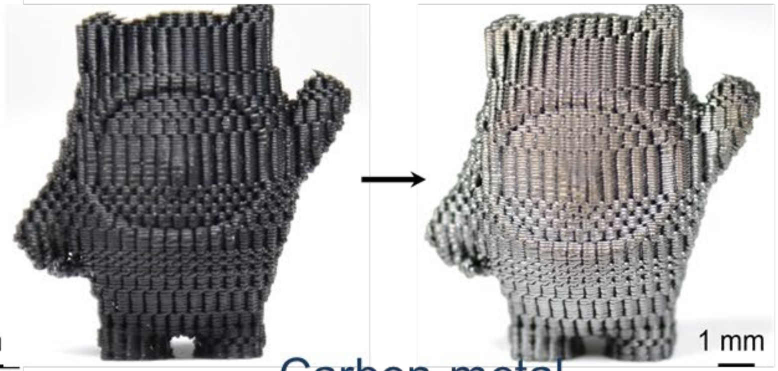
Composites





Carbon-epoxy

Carbon-metal

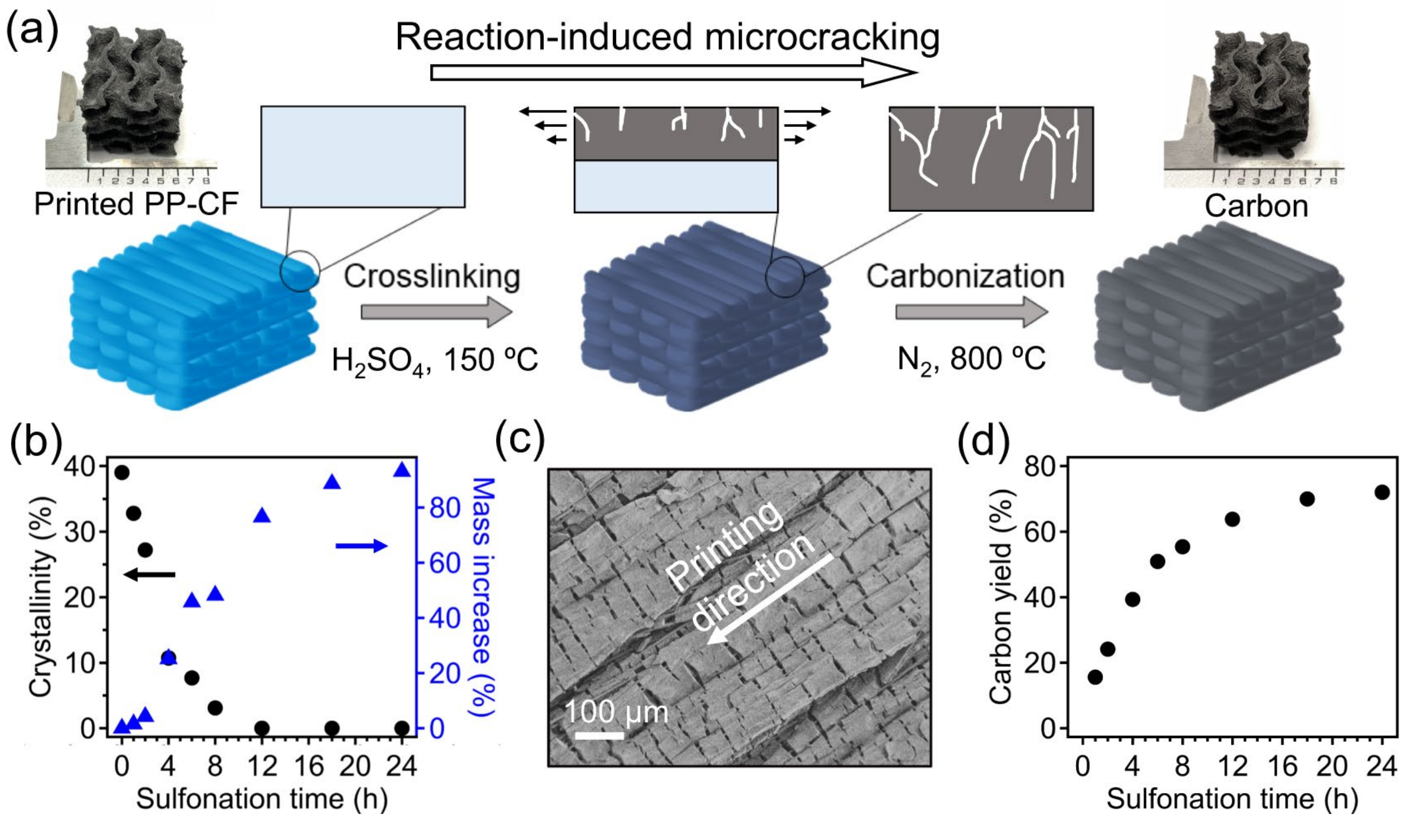


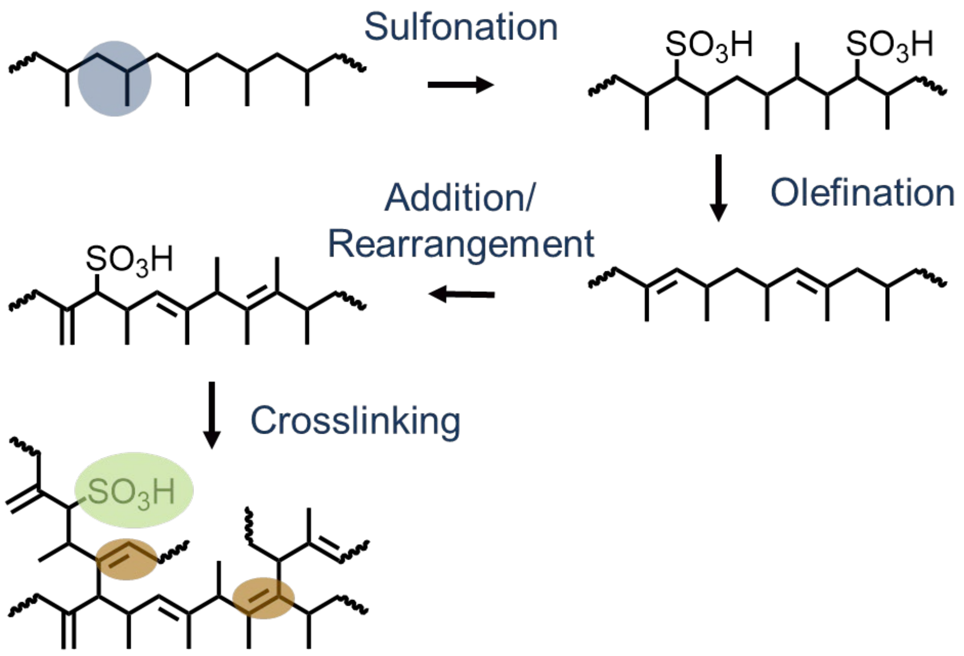
Carbon-metal

Advanced Materials, 2023, 35(38)

Polyolefin-derived Carbons to Enhance Coal Carbon Bonding

Core technology: Sulfonation-induced crosslinking and thermal stabilization





Nature Communications, 15, 838 (2024)

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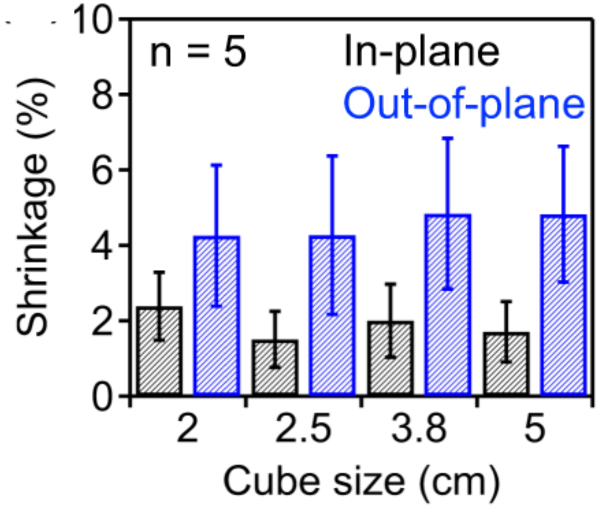
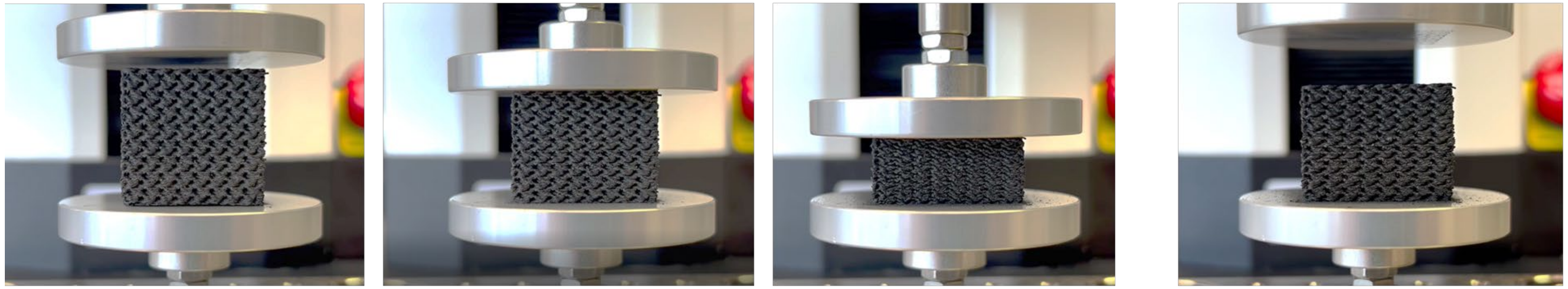
Controlled Carbon Density and Mechanical Properties

8 g carbon holding 100 kg weight

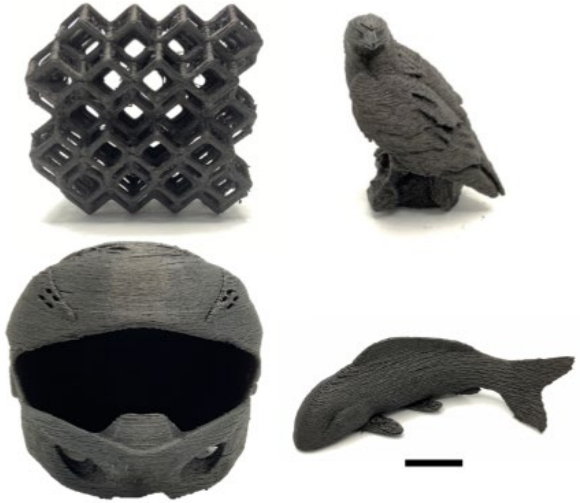


Compression

Release



0% strain | 16% strain | 50% strain | ~90% recovery



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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/copper particles to improve structural integrity.
2. **Increasing the density** of the carbon/copper scaffold to achieve greater material robustness.
3. **Improving the printability** of high C/Cu-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.

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. **Developing coal/metal filaments for 3D printing.**
3. **Launching a specialized extruder head**, uniquely engineered for the efficient 3D printing of high carbon-loaded filaments, thereby meeting a specific market need.
4. **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.

Summary

1. Filaments composed of coal-derived graphene and polypropylene (PP) have been successfully fabricated and subjected to testing.
2. The addition of copper nanopowders into these filaments is the next step, and preparations are underway for testing this enhancement.
3. Polyacrylonitrile (PAN) is poised to be incorporated into the carbonized carbon scaffold to improve its mechanical properties.

Acknowledgement

- Team members
- Program manager: Sandy J Napolitano

Thank you!

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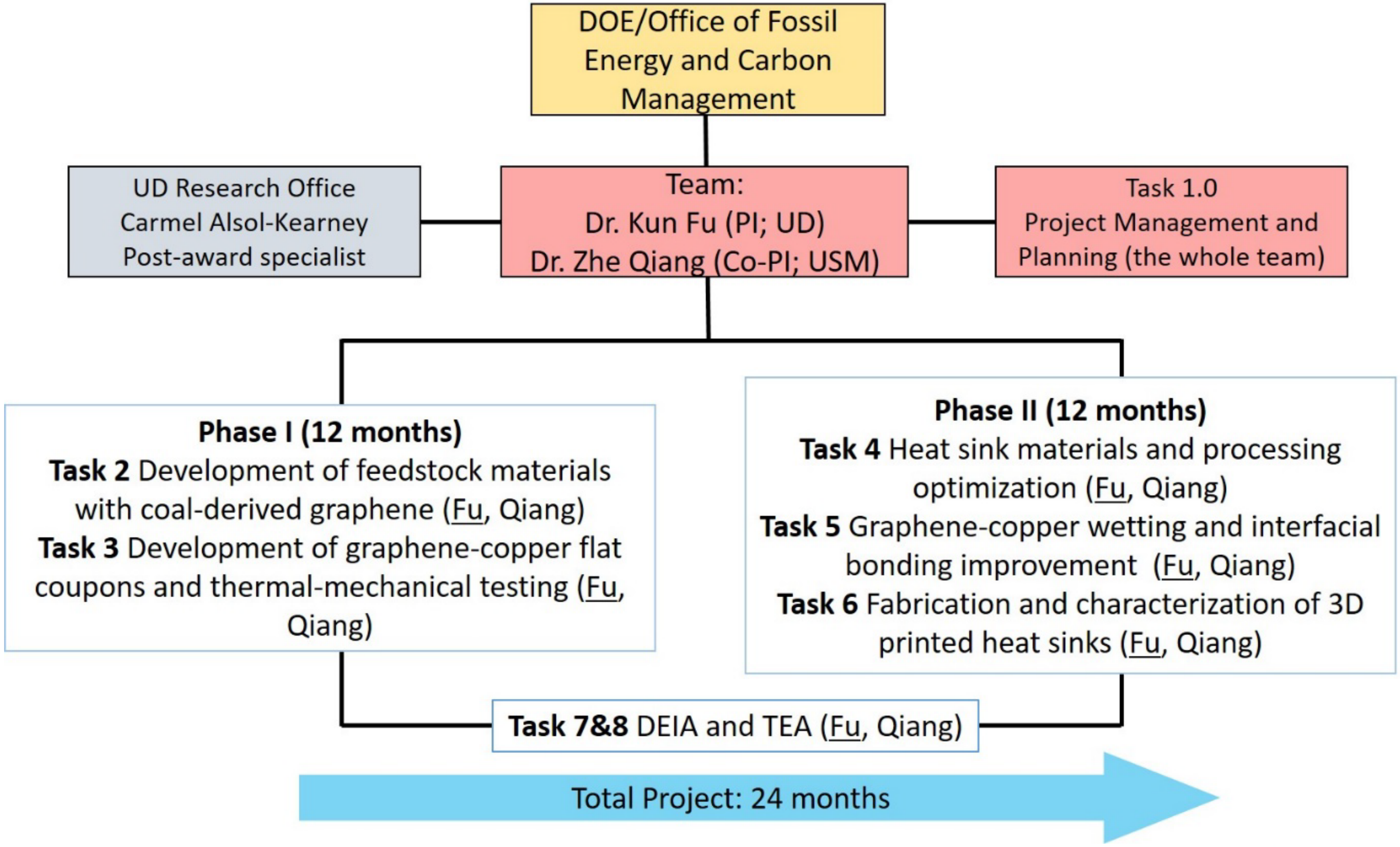
Project Organization and Management Structure



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Project Schedule