1T-MoS₂ Fibers for Flexible Energy Storage: A Bit of a Stretch?

Lucija Koledic, Sophie Mance, Dr. Ye Wang*, Prof. Manish Chhowalla*

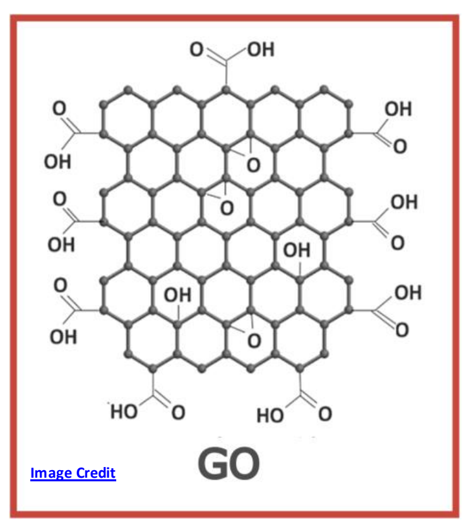
1. Introduction

Abstract & Motivation

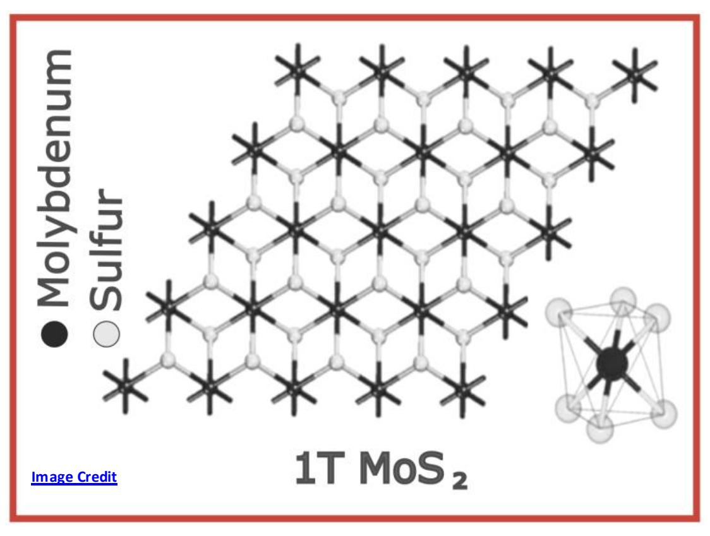
The rapid growth of portable electronics calls for the development of flexible components, including the power supply unit. Fiber-shaped materials exhibit the potential to be incorporated into woven textiles ideal for wearable devices.

In this work, we develop a strategy for forming flexible anode materials from fibers of two-dimensional (2D) materials. These two-dimensional nanosheets form thin fibers in a coagulation bath, reaching diameters down to 100 µm. The fibers show high conductivity up to 4.6 Siemens/meter, demonstrating their potential for future applications in flexible batteries.

2D Materials in Fibrous Battery Anodes



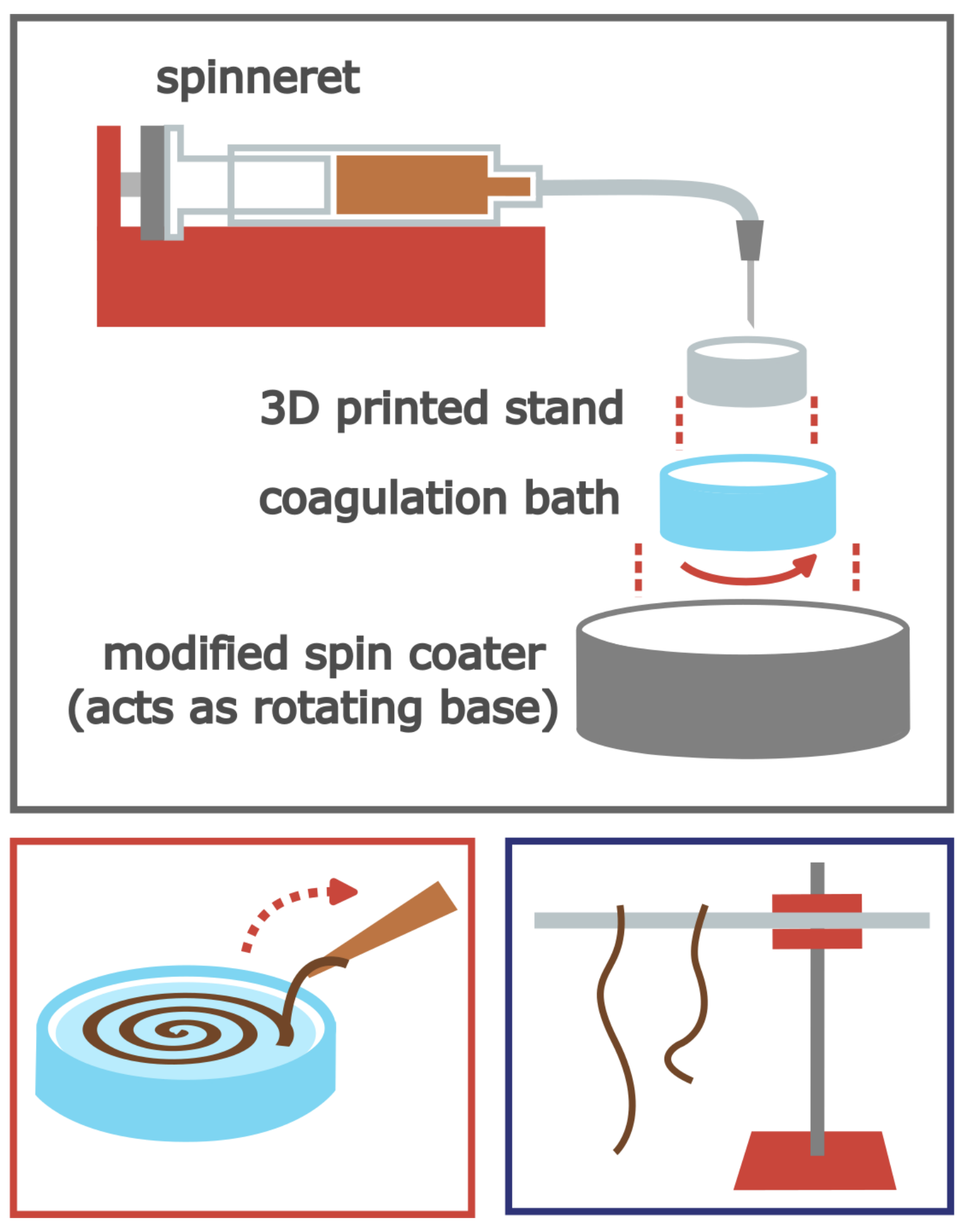
2D material fibers have previously been formed with **graphene oxide (GO)**, however this material is **non-conductive** due to its lack of an efficient carrier transport mechanism (few pathways between sp^2 carbon clusters).[2 3]



While MoS_2 naturally occurs in the semi-conductive 2H phase, **metastable 1T MoS_2** exhibits conductivity despite its atomically thin structure.[1]

To maintain a fibrous shape while also achieving high conductivity, we mix GO with 1T-MoS_2 to form a composite.

Fabrication of Fibers via Coagulation



1. Gel Formation

- Sol-gel synthesis
- Material must surpass certain concentration to be successfully spun due to **Onsager's theory:**

Liquid crystals (LCs) approximated as hard rods will transition from isotropic to nematic as LC density increases

- Can extend to high alignment in 2D materials, which similarly have a high aspect ratio [4]

2. Extruding gel in coagulant ("wet-spinning")

- Forces formation and alignment of stream of negatively charged 2D sheets in parallel
- Coagulant initiates ionic cross-linking as cations diffuse into the gel's inner structure and undergo electrostatic attraction [3]

3. Retrieving fibers and hanging to air-dry

2. Methods and Results

Aims:

- **Create a control group to compare with MoS_2 + GO fibers**
- **Determine ideal parameters for fiber formation process**

Departing material:
Sol-gel GO stock solution (aq, ≈5µg/mL) in 0.5 mm syringe

Parameters to determine

1. Coagulating cation (Ca^{2+}, Fe^{3+}, Na^+, Ni^{2+}): Balance between intercalating cation size and degree of ionic bonding character.
2. Coagulation bath solvent
3. Injection rate of spinneret
4. Rpm of rotating base

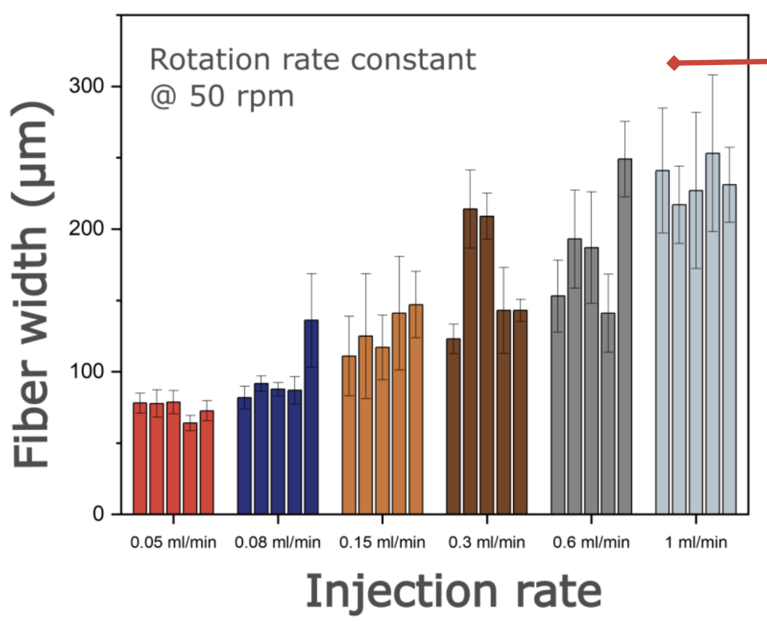
1. 5wt% $CaCl_2$ chosen for higher observed rate of successful fiber extraction.
2. 3:1 water:ethanol used to tailor density and force fibers to sink before tangling

High injection rate → high drag with needle → higher forced alignment of sheets → stronger fibers

High injection rate → thicker and heavier fiber → likely to break on extraction

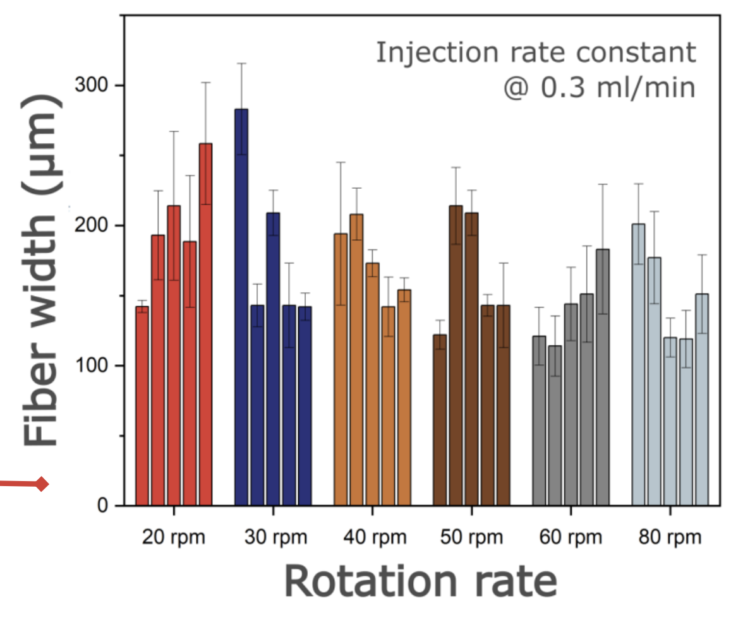
No significant quantitative correlation between rotation rate and fiber width

Qualitatively, it was observed that a low rotation rate could lead to tangling in the spun fiber, while a high rate could lead to tight coiling.

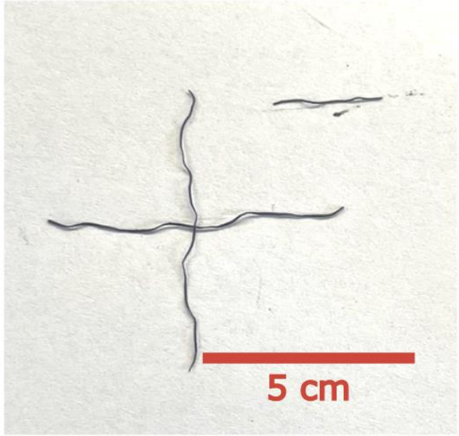


3. 0.3 ml/min chosen for good balance between alignment and thickness

4. 50 rpm chosen for optimum coiling



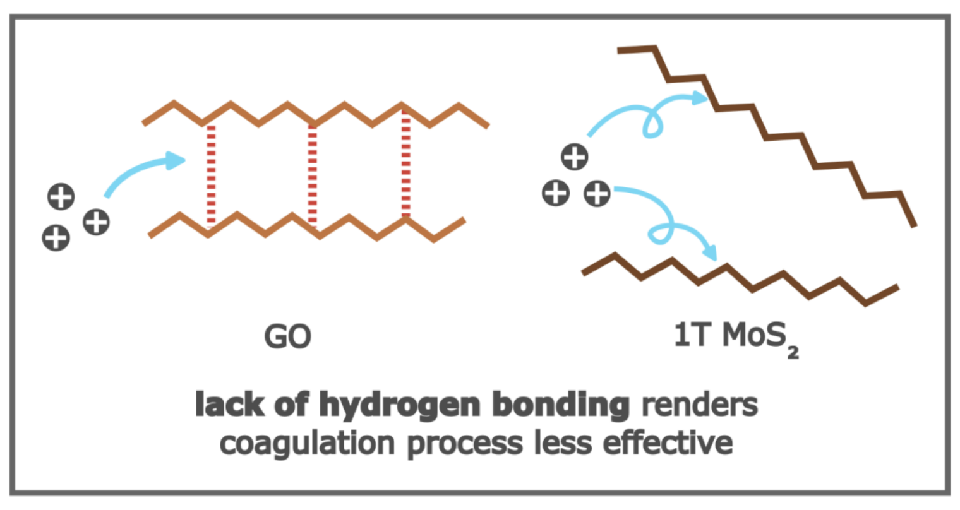
GO Fibers



resulting GO fibers

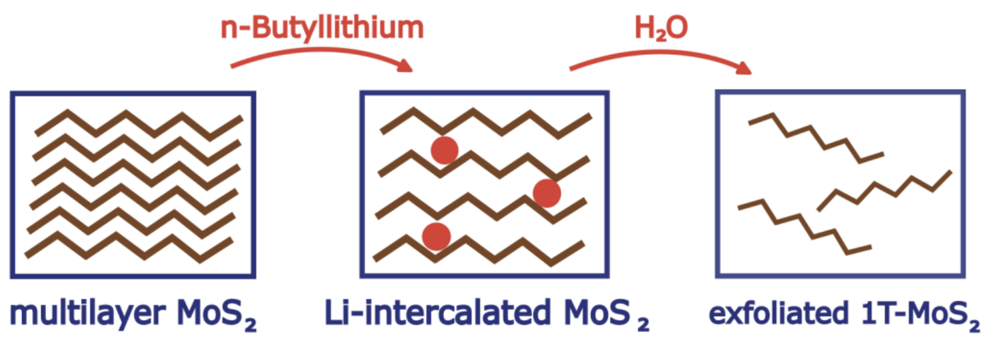
MoS₂ Fibers

Unlike GO, MoS_2 cannot form fibers on its own, suggesting **gelation with water by hydrogen bonding is key to fiber coagulation.** The lack of hydroxyl groups on MoS_2's surface hinders inter-planar interaction during the coagulation process, leading to fewer chances for successful ionic cross-linking. **We adapt by using GO as a gelation agent to form composite GO/MoS_2 fibers.**

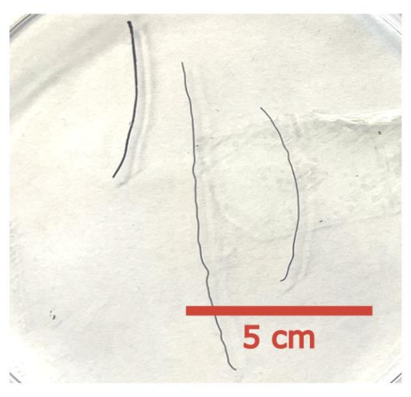


lack of hydrogen bonding renders coagulation process less effective

1. Li-intercalation assisted exfoliated 1T MoS_2 (Li-MoS_2): Top-down approach

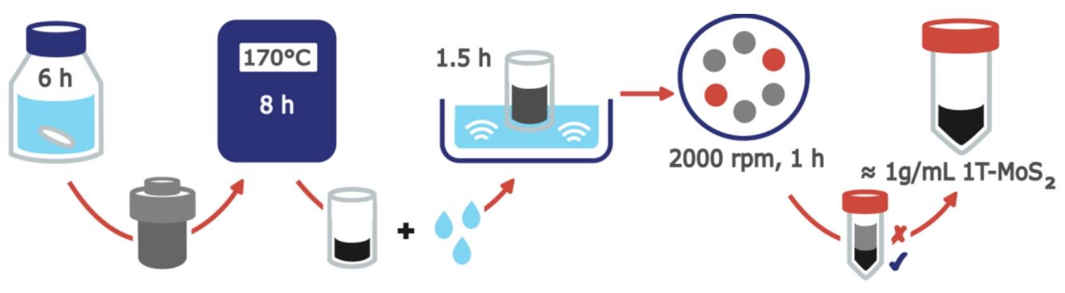


1:2 volume ratio Li-MoS_2:GO mixture → 1.5 hr sonication → gel



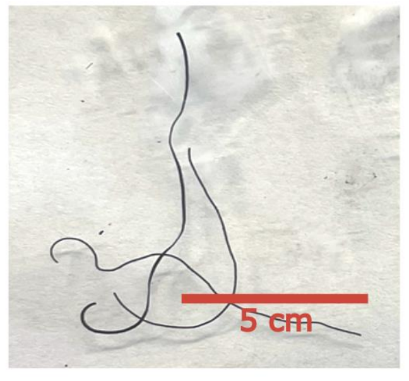
Li-MoS_2 fibers

2. Hydrothermal Synthesis 1T MoS_2 (HT-MoS_2): Bottom-up approach [5]



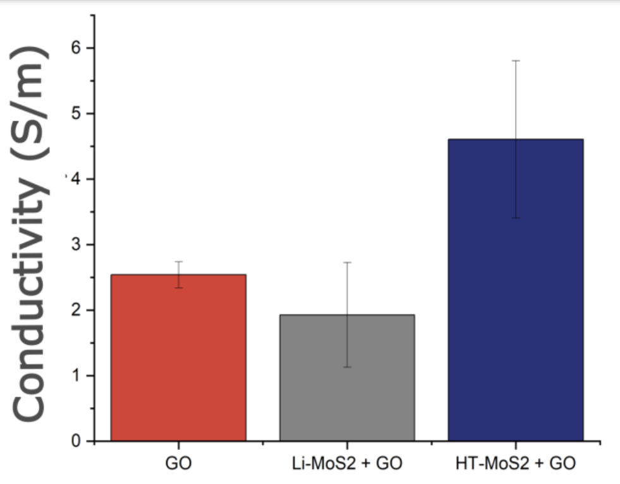
$$MoO_3 + 3CH_3CSNH_2 + NH_2CONH_2 + 5O_2 \rightarrow MoS_2 + CH_3CONH_2 + (NH_4)2S + N_2\uparrow + 5CO_2\uparrow + 3H_2O$$

1:2.5 volume ratio HT-MoS_2:GO mixture → 1.5 hr sonication → gel



HT-MoS_2 fibers

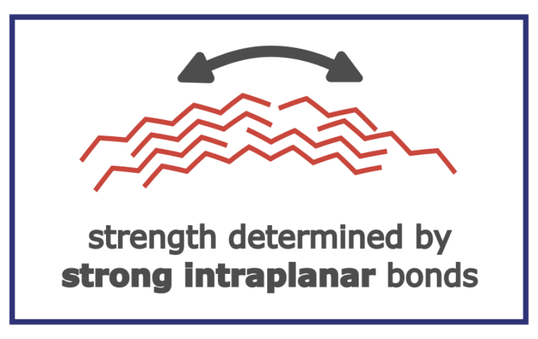
Electrical Properties



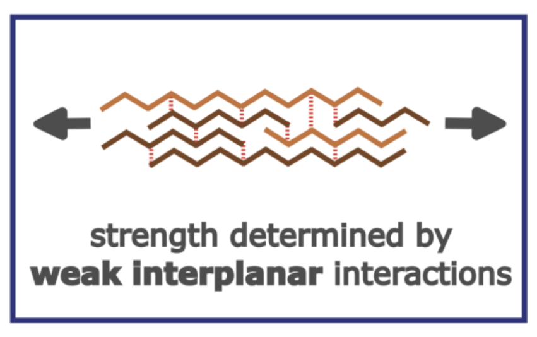
Higher conductivity is observed in HT-MoS_2, likely due to the rich hydroxyl functionality on the surface. This results in **stronger inter-planar interactions in the fiber network** which facilitates electron transport in the fibers.

Mechanical Properties

While the fibers were too fine to successfully perform quantitative mechanical tests, all fibers were found to be strong under bending moments but weak in tension. This is explained by considering sheet orientation within the fiber:



strength determined by **strong intraplanar** bonds



strength determined by **weak interplanar** interactions

Conclusion & Next steps

- GO/ 1T MoS2 fibers were successfully fabricated by wet-spinning.
- Fibers with hydrothermally synthesized 1T-MoS_2 nanosheets show higher conductivity, making them a promising option for flexible battery anodes

Future plans:

- Improve HT-MoS2 yield (currently **28% success rate** due to sensitivity of MoS2 phase transformations to temperature and pH) [6]
- Stock GO gel used was two years old, which can lead to partial reduction in the material,[2] contributing to increased conductivity but lower mechanical strength [7] → synthesize fresh batch of GO to investigate balance between conductivity and mechanical strength

References

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Intern bio

Lucija is a Physical Natural Sciences student starting her second year at the University of Cambridge. She completed this work as part of the Department of Materials Science and Metallurgy's 2DMD group.

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