

Dynamic in-situ experiments utilizing probe microscopy

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Graphene flakes floating on molten gold

MOTIVATION

Graphene is probably the most well-known two-dimensional material, and it is especially interesting because of its electronic properties. For example, graphene possesses very high electron and hole mobilities. However, achieving the desired electronic properties is only possible under one critical assumption: the graphene must not have any defects in its lattice. The most common type of defect occurring during graphene growth by the chemical vapour deposition is the *grain boundary* (see Figure 1a). This issue could theoretically be overcome by growing graphene on a liquid substrate like liquid gold (see Figure 1b) as the grains could align with each other (see Figure 1b).

However, previous research (M. Jankowski, ACS Nano vol. 15, 2021) has shown that the reality is more complicated and the force interaction between the grains is more complex. The capillary action, which would be accompanied by the presence of meniscus around the graphene grains (see Figure 2), was suggested as one of the forces present. I utilised atomic force microscopy (AFM) to confirm or disprove the presence of the meniscus.

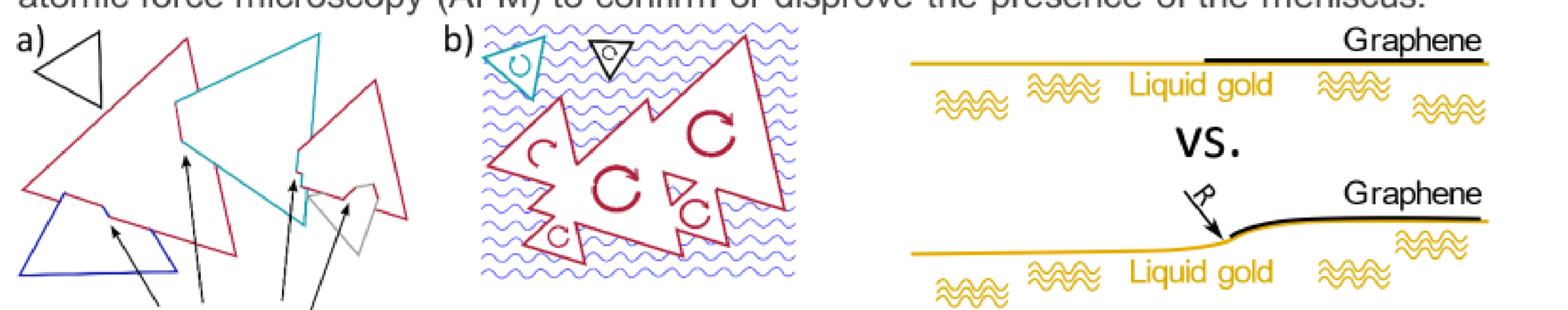


Figure 1: Graphene grown on solid (a) vs liquid (b) substrate. Image courtesy of M. Kolibal.

Figure 2: Graphene flake without (top) and with (bottom) a meniscus around it.

Electrodeposition on a solid-state battery

MOTIVATION

Electrodes in a battery are separated by an electrolyte, which is an ion-conductive material with minimal electron conductivity. Electrolytes do not store energy, but they are often the determining factor for cell safety and the development of new types of batteries is often dependent on finding a suitable electrolyte. Unlike the more common liquid electrolytes used in contemporary Li-ion batteries, solid electrolytes could enable the utilisation of electrode materials with greater capacity and the production of cells with better safety characteristics. As these electrolytes often have fairly heterogeneous microstructure, AFM can be useful to investigate local conductive properties of the electrolytes.

I utilised an AFM-in-SEM microscope LiteScope to probe local ionic conductive properties of the $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte by electrodepositing lithium pillars on top of the electrolyte by conductive AFM (see Figure 1).

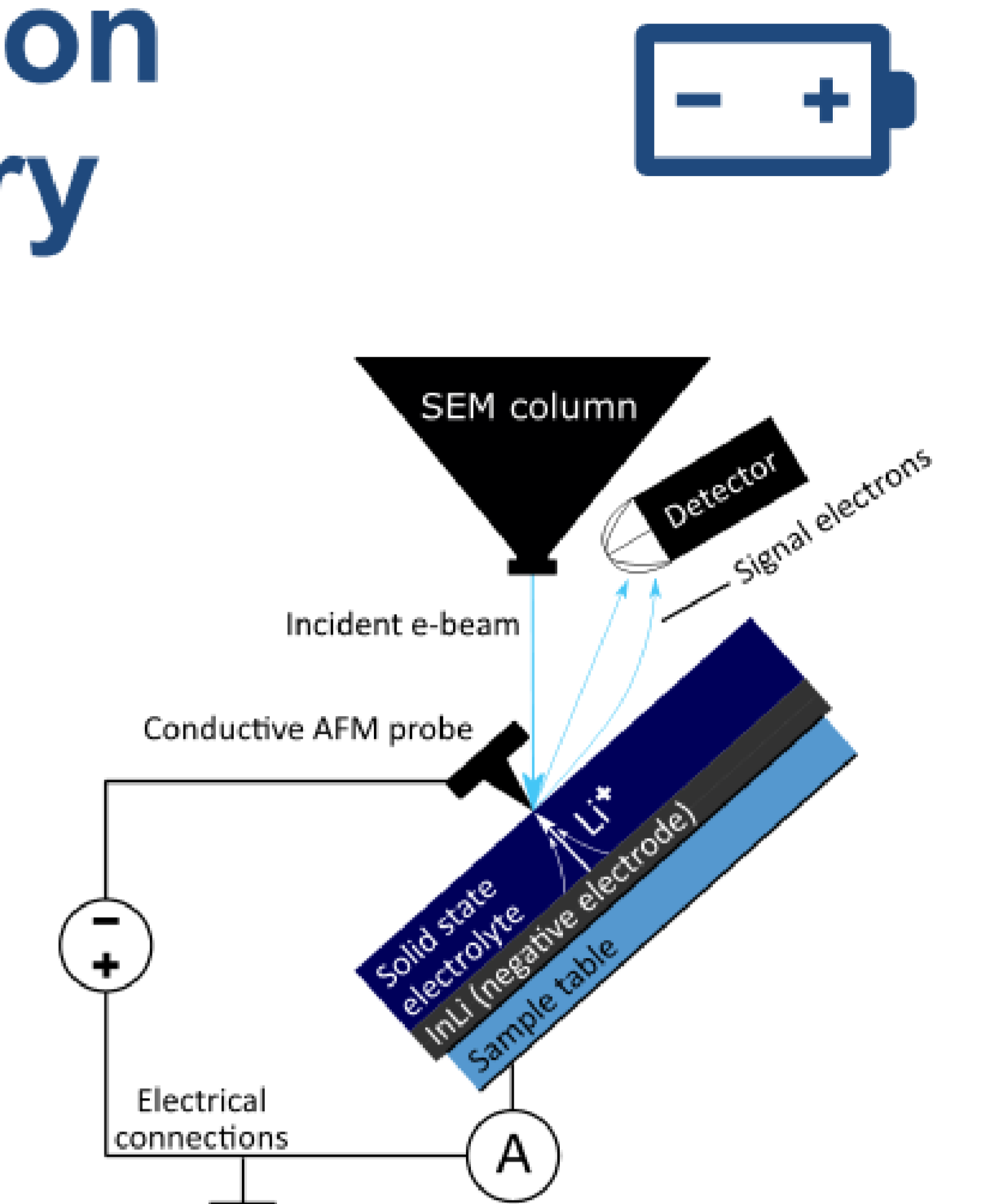
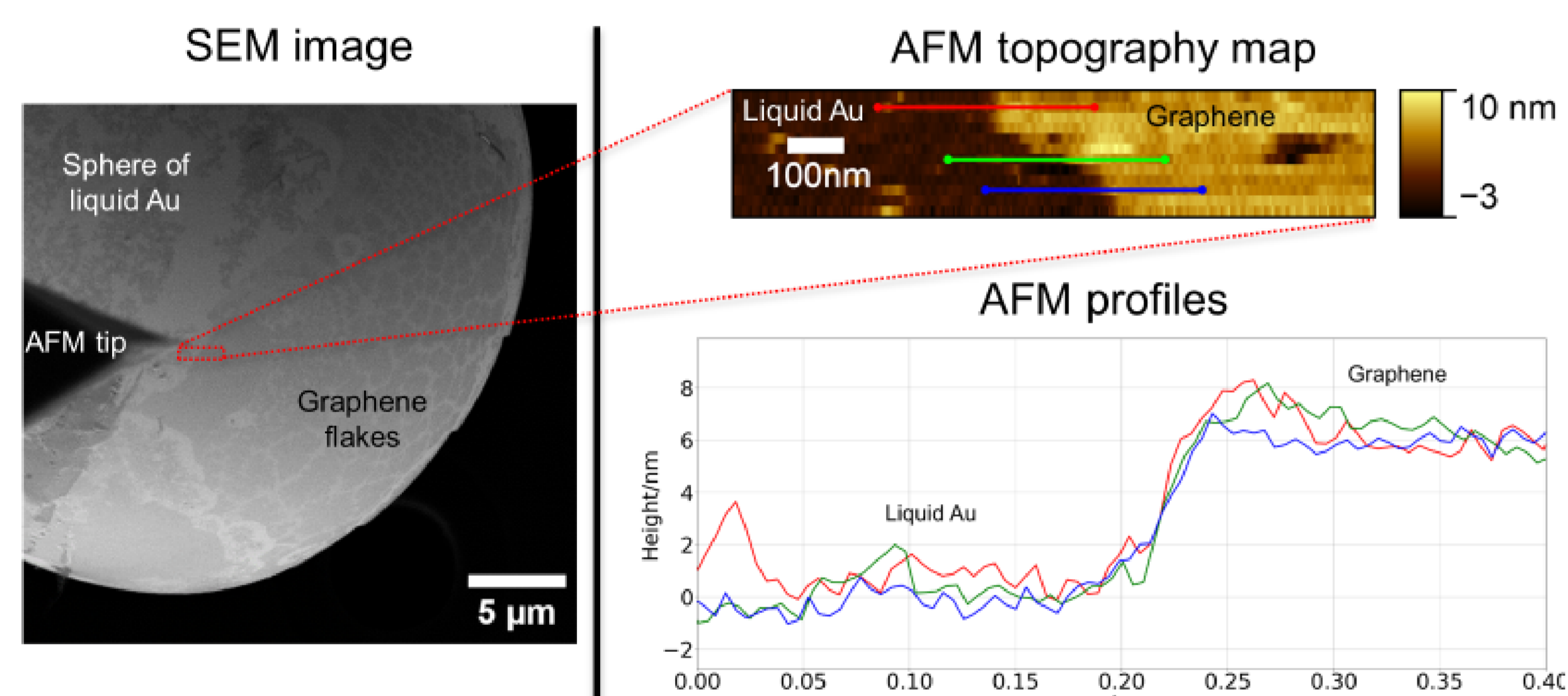


Figure 1: The experimental setup. The AFM probe has a negative bias, and therefore lithium ions are driven through the electrolyte from the negative electrode to the AFM probe.

Graphene flakes floating on molten gold

RESULTS



I utilised the AFM microscope LiteScope designed for integration with a scanning electron microscope (SEM) to image edges of graphene. The measurement consistently showed that the offset between gold and graphene is very small and the size of the meniscus is insignificant.

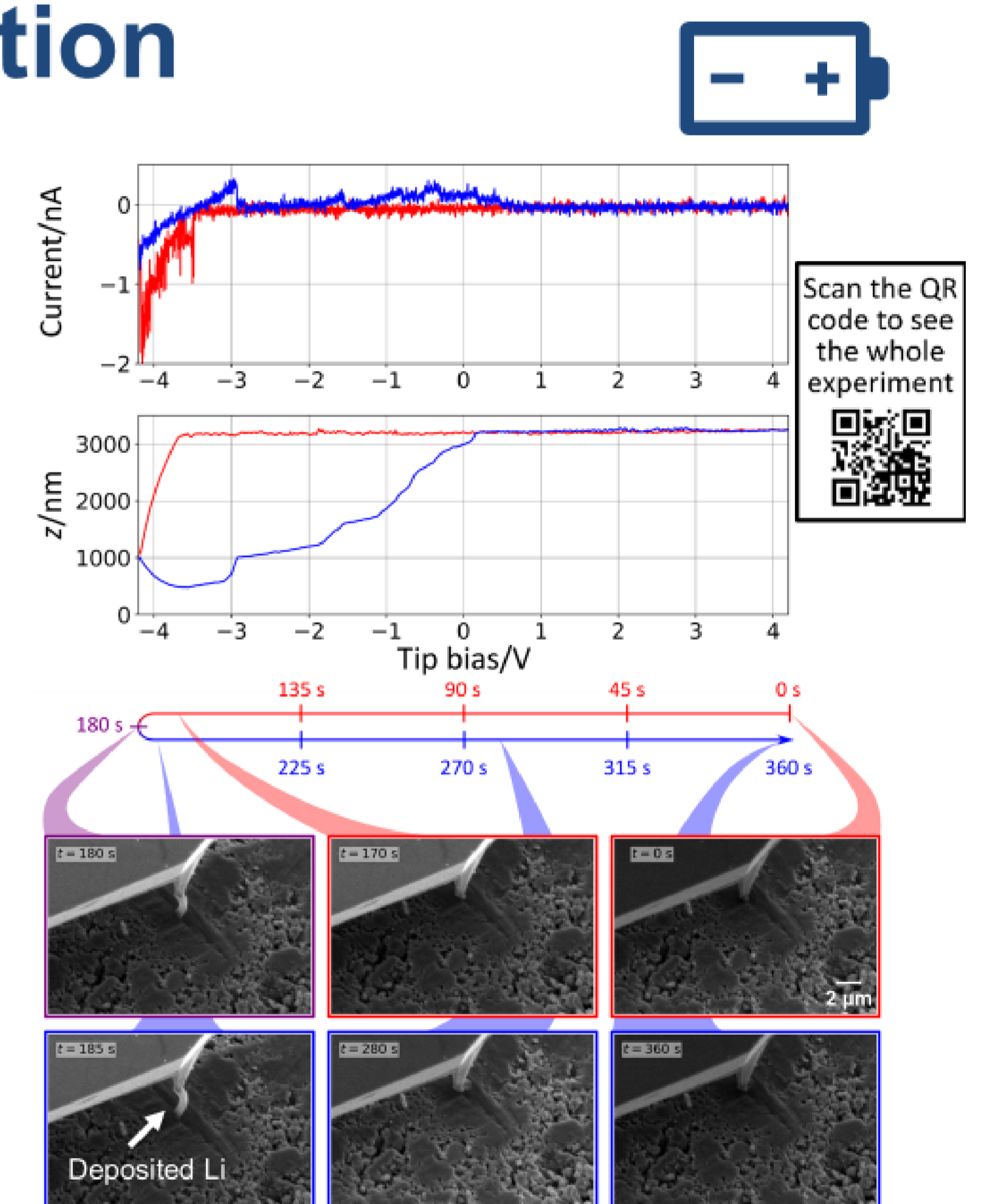
Electrodeposition on a solid-state battery

RESULTS

A conductive AFM probe was positioned on top the electrolyte and an IV spectroscopy of the tip bias was performed while the sample was grounded. The sweep started with a positive bias of 4.4 V applied to the probe. The bias then decreased linearly with time until the voltage -4.4 V was reached and lithium deposited. At this point, the process reversed and the voltage was increased back from -4.4 V to 4.4 V to drive lithium back.

An unsuccessful experiment in which a wide IV sweep (10 V to -10 V) caused a very large pillar to deposit.

An unsuccessful experiment in which the conductive contact between the pillar and the electrolyte was lost.

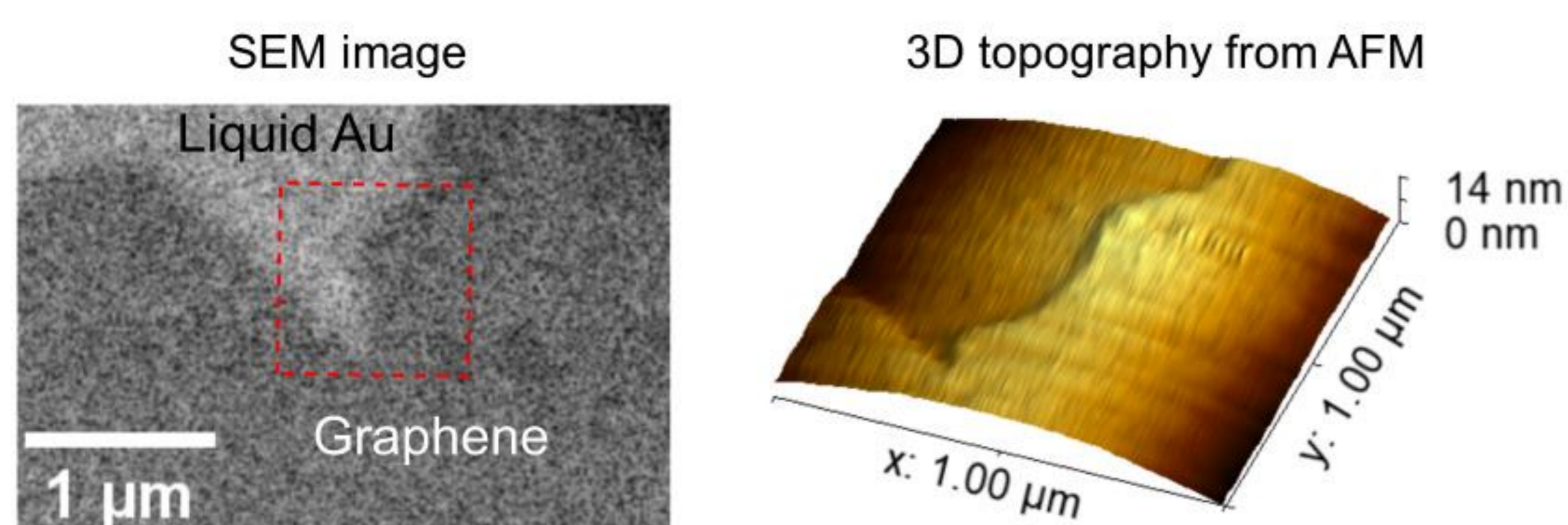


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CONCLUSIONS

In an effort to explain the force interactions that take place between flakes of graphene floating on top of molten metals, I have built upon the work of other scientists. My measurements do not support the presence of any significant meniscus (larger than units of nanometres) around the graphene flakes. Capillary action is therefore not present in the system and the interactions taking place in the system must be described by other forces.

Beyond the study of the graphene-on-liquid system, this kind of measurement also holds interest from the instrumentation perspective. Scanning probe microscopy on liquid surfaces is generally considered difficult, and it is important to know that it is possible on liquid gold.



Electrodeposition on a solid-state battery

CONCLUSIONS

In these experiments, I investigated the electrodeposition of lithium in a half-cell (a battery with the positive electrode missing). I used the probe tip as a current collector and electrodeposited lithium pillars on top of the solid electrolyte. I was able to perform the deposition repeatedly, with lithium migrating from the negative electrode to the probe and subsequently fully returning to the negative electrode.

These experiments demonstrate a possible use-case for conductive AFM as a tool for probing the conductive properties of solid electrolytes. Such experiments can be used to study the characteristics of composite solid electrolytes, potentially revealing variations in conductivity among the individual phases.

