

Scanned probe microscopy studies of MoS₂ catalysis on insulating substrates: impact of substrate, strain, and defects

Shawna Hollen, University of New Hampshire

Project background

Despite more than 50 years of industrial use, the fundamental mechanisms for the hydrodesulfurization (HDS) reaction on MoS₂ and, in particular, the importance of the two-dimensional nature of the catalysts have only started to be understood in the last decade. Due to their performance and natural abundance, MoS₂ and WS₂ catalysts have been used on an industrial scale for HDS of oil feedstock since World War II.(1,2) Environmental concerns are now prompting stricter government regulations and motivating ultra-deep sulfur removal from petroleum products. Improved catalyst design is increasingly important for efficient and responsible use of our natural resources. This design has long been guided by large-scale, mostly spectroscopic experiments and trial-and-error. Our current PRF-funded project aims to achieve a deeper understanding of the catalytic process by using experimental probes approaching the atomic scale.

Our specific project objectives are to find absorption sites of a thiophene test molecule on MoS₂ using insulating substrates. Previous scanning tunneling microscopy (STM) experiments found that thiophene adsorbs and decomposes on MoS₂ edges.(3) These experiments showed how useful scanning probe techniques can be in understanding catalysis and had a great influence on industry. However, they were all performed on nanoscale MoS₂ crystals grown in ultra-high vacuum on gold substrates—samples that are far from industrially relevant. Our work complements and extends these experiments by studying MoS₂ catalysis using insulating substrates and exfoliated samples that are more closely related to those used in industry. Using a novel aluminum oxide substrate, we will also be able to directly probe the effects of crystalline strain, which is expected to improve MoS₂'s reactivity.(4) These investigations could significantly impact our understanding of catalysis in MoS₂, especially how it depends on substrate and strain.

Experimental systems development

Moving to an insulating substrate creates some experimental challenges, to which we have taken different approaches for each of our experimental systems. Our first target is MoS₂ flakes exfoliated onto SiO₂/Si substrates: a typical sample for prototype 2D material electronic devices. Because these flakes are islands on an insulator without a current path to ground, we probe these samples using qPlus atomic force microscopy (qPlus AFM) instead of STM (see Fig. 1). Since the scan range of this instrument is ~1 μm at low temperature and ~10 μm at room temperature, finding flakes of interest is very time consuming. To accelerate the process, we employ a TEM shadow mask technique to create a visible grid of 50 μm gold squares on the surface to navigate the tip to within 15 μm of the target flake (Fig 1a,b). In the future, it should be possible to use this technique to make electrical contact to flakes,

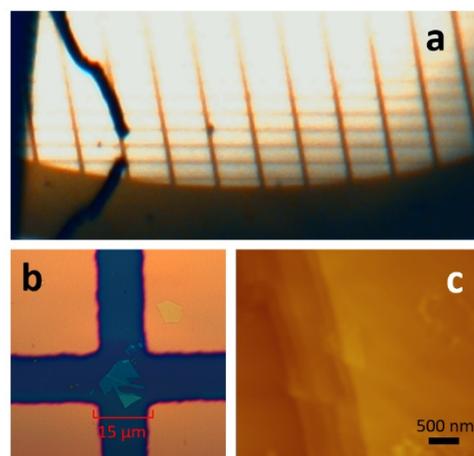
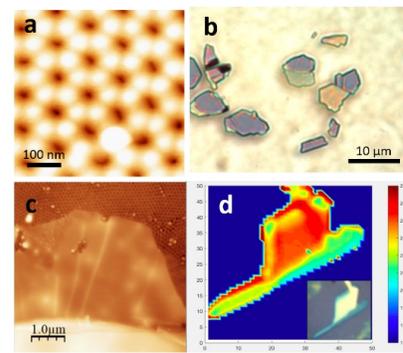


Figure 1: qPlus AFM experiments on MoS₂ flakes, a) SiO₂/Si substrate with exfoliated flakes and an evaporated Au grid. b) Optical microscope image of target flake in grid crosshairs. c) qPlus AFM image of flake edge at 80 K.

which would enable combined STM/AFM. Finally, it is very important to maintain pristine surfaces, so we avoid lithography and solvent processing methods and we anneal samples in vacuum at 130°C before imaging.

Our second target system is MoS₂ on anodized aluminum oxide (AAO). As shown in Fig. 2, AAO is a nanostructured substrate with ~20 nm undulations surrounding 50 nm holes that are spaced by ~100 nm. We expect this substrate to induce strain in the MoS₂ sheet while still being suitably smooth for scanned probe imaging techniques. If the MoS₂ is strained at the hillocks, we expect to see an adsorption preference there for thiophene. In addition, because of the holes, this substrate offers an opportunity to compare activity in suspended versus supported MoS₂.



surface. b) Optical image of MoS₂ flakes exfoliated onto AAO. c) AFM image of an MoS₂ flake on AAO. d) Raman mapping of MoS₂ flake on SiO₂/Si. Colormap shows the energy difference between the A_{1g} and E_{2g} modes.

Experiments in progress

Experiments are underway to probe the adsorption of thiophene onto exfoliated MoS₂ flakes on SiO₂/Si substrates. We imaged few-layer flakes on a micron scale (see Fig. 1c) and saw preliminary evidence of thiophene collecting on the edges of flakes after heavy dosing at 80 K. The adsorption and decomposition are both temperature dependent, and these parameters need to be explored. Additionally, it was important in the original experiments to pre-treat the MoS₂ with atomic hydrogen to get thiophene to react with MoS₂.⁽⁵⁾ Finally, we are currently limited by the resolution we can achieve with our qPlus microscope. This limit is partly because the large-scale imaging (1-10 μm) that is necessary for finding our samples often negatively affects our tip, reducing its radius of curvature and therefore the resolution possible. All these factors can be addressed now that we have designed a better experimental system, have the prospect of doing both STM and AFM, and have a newly installed heater in our prep chamber that will enable the hydrogen-based experiments.

In parallel, we have been developing the AAO/MoS₂ experimental system. Two undergraduate students have worked on exfoliating and characterizing flakes of MoS₂ on AAO. Various standard methods have been tried, including tape, PDMS, and polymer transfer, with surprisingly limited success. Tape exfoliation has been the most successful, producing small and relatively thick flakes. We have used AFM imaging and Raman spectroscopy to characterize these samples, as shown in Fig. 2. Some evidence of strain is there, but it will be far preferable to achieve a sample that is a continuous sheet of material on AAO. This effort is continuing and forms the basis of one undergraduate's proposal to the Hamel Center for Undergraduate Research as a semester-long research effort.

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