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Scanned probe microscopy studies of MoS_2 catalysis on insulating substrates: impact of substrate, strain, and defects

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Project background

Despite more than 50 years of industrial use, the fundamental mechanisms for the hydrodesulfurization (HDS) reaction on MoS_2 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, MoS_2 and WS_2 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 MoS_2 using insulating substrates. Previous scanning tunneling microscopy (STM) experiments found that thiophene adsorbs and decomposes on MoS_2 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 MoS_2 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 MoS_2 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 MoS_2's reactivity.(4) These investigations could significantly impact our understanding of catalysis in MoS_2, 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 MoS_2 flakes exfoliated onto SiO_2/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, which would enable combined STM/AFM. Further efforts in this direction include using new methods to create large-area MoS_2 on insulating substrates (Figure 2a) and to pattern a grid of gold arrows around an MoS_2 flake of interest (Figure 2b). Additionally, improved imaging with the qPlus AFM allows us to differentiate between SiO_2 and evaporated gold by examining the surface topography (Figure 2c-e).

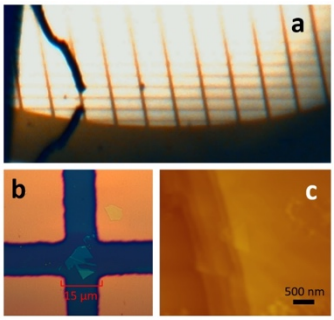

Figure 1: qPlus AFM experiments on MoS_2 flakes, a) SiO_2/Si substrate with exfoliated flakes and an evaporated Au grid. b) Optical microscope image of target flake in grid crosshairs. c) qPlus AFM image of flake edge at 80 K.

Our second target system is MoS_2 on anodized aluminum oxide (AAO). As shown in Figure 3, 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 MoS_2 sheet while still being suitably smooth for scanned probe imaging techniques. If the MoS_2 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 MoS_2.

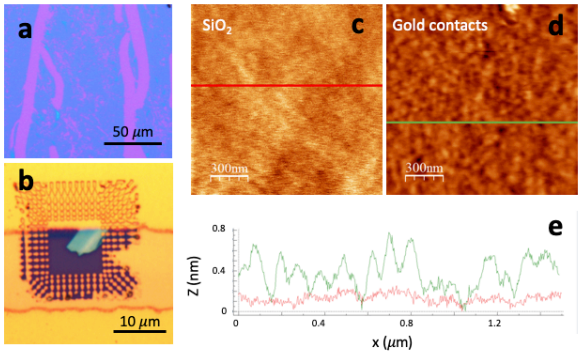

Figure 2: MoS_2 sample generation and identification for qPlus AFM experiments. a) Large area, single layer MoS_2 on SiO_2. b) MoS_2 flake patterned within a gold grid of arrows. c) and d) qPlus AFM on SiO_2 and gold contacts, respectively. e) topography line scans showing the variation in surface roughness on SiO_2 and gold.

Experimental progress

We have performed experiments to probe the adsorption of thiophene onto exfoliated MoS_2 flakes on SiO_2/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 MoS_2 with atomic hydrogen to get thiophene to react with MoS_2.(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/MoS_2 experimental system. Two undergraduate students have worked on exfoliating and characterizing flakes of MoS_2 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.

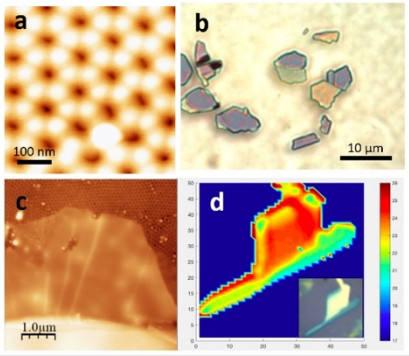

Figure 3: a) AFM image of bare AAO surface. b) Optical image of MoS_2 flakes exfoliated onto AAO. c) AFM image of an MoS_2 flake on AAO. d) Raman mapping of MoS_2 flake on SiO_2/Si. Colormap shows the energy difference between the A_{1g} and E_{2g} modes.

Further progress has been hampered by two unexpected obstacles. First, the imaging is much more difficult than we expected, and we are still learning this advanced technique. Second, and most significantly, our instrument was catastrophically damaged by poorly regulated power two years in a row, resulting in more than 6 months of down time. We are therefore still executing the planned experiments.

1. H. Topsøe, B.S. Clausen, and F.E. Massoth. in *Catal. Technol. Vol. 11*, edited by J.R. Anderson and M. Boudart (Springer Berlin Heidelberg, Berlin, Heidelberg, 1996)https://doi.org/10.1007/978-3-642-61040-0
2. A. Stanislaus, A. Marafi, and M.S. Rana. Recent Advances in the Science and Technology of Ultra Low Sulfur Diesel (ULSD) Production. *Catal. Today*, **153**, 1 (2010). https://doi.org/10.1016/j.cattod.2010.05.011
3. J.V. Lauritsen and F. Besenbacher. Atom-Resolved Scanning Tunneling Microscopy Investigations of Molecular Adsorption on MoS2 and CoMoS Hydrodesulfurization Catalysts. *J. Catal.*, **328**, 49 (2015). https://doi.org/10.1016/j.jcat.2014.12.034
4. J.H. Lee, W.S. Jang, S.W. Han, and H.K. Baik. Efficient Hydrogen Evolution by Mechanically Strained MoS_2 Nanosheets. *Langmuir*, **30**, 9866 (2014). https://doi.org/10.1021/la501349k
5. J. V. Lauritsen, M. Nyberg, J.K. Nørskov, B.S. Clausen, H. Topsøe, E. Lægsgaard, and F. Besenbacher. Hydrodesulfurization Reaction Pathways on MoS2 Nanoclusters Revealed by Scanning Tunneling Microscopy. *J. Catal.*, **224**, 94 (2004). https://doi.org/10.1016/j.jcat.2004.02.009