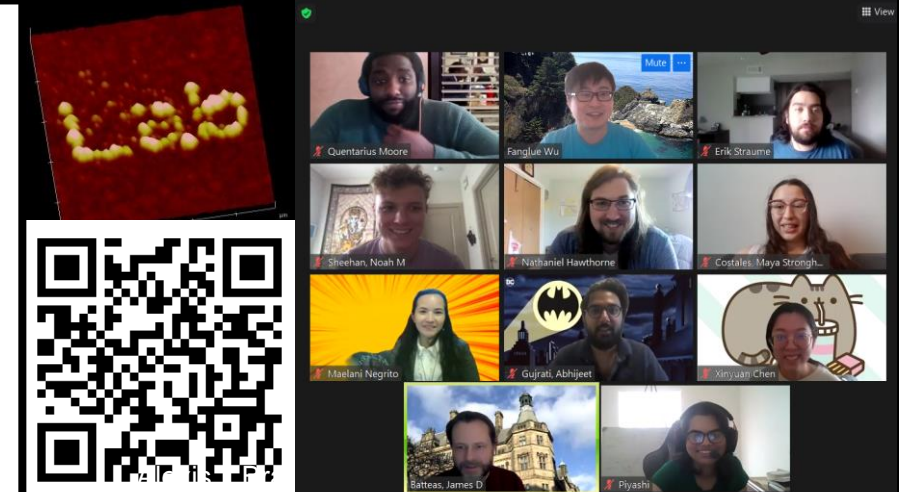


Materials Chemistry at Surfaces and Interfaces

-basic science for real world challenges

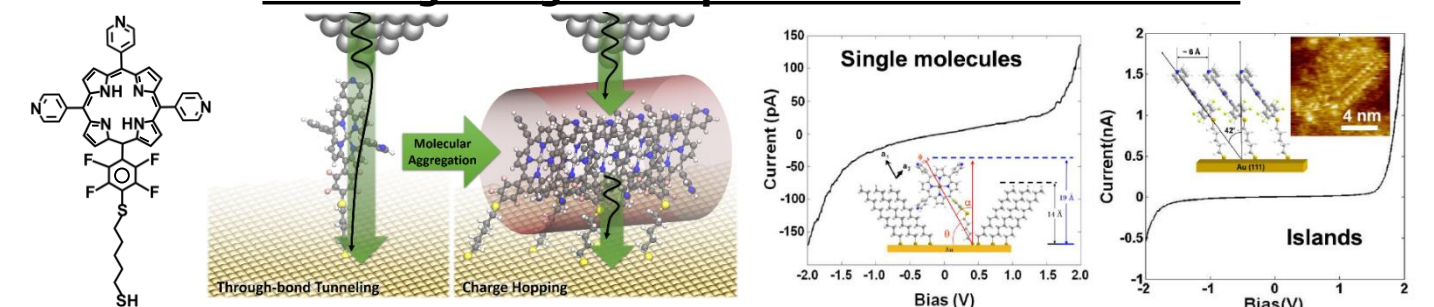


The research in our group is organized around two main projects: 1) **Nanoscale materials and devices** – with a focus on architected materials for novel electronics and energy storage systems and 2) **Nanotribology** – where we are seeking to understand the atomic scale origins of friction, and to utilize this to control friction across scales, from nano-devices to machined interfaces, in mechanically driven chemical reactions, and even up to the role of friction and tribochemistry in earthquakes. Our work is centered on obtaining a fundamental (molecular level) understanding of the underlying chemistry and physics of the systems in question to afford rational approaches to test and develop new technologies. In much of our research we employ a range of scanned probe microscopies such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) to probe structure and to manipulate materials at the nanoscale.

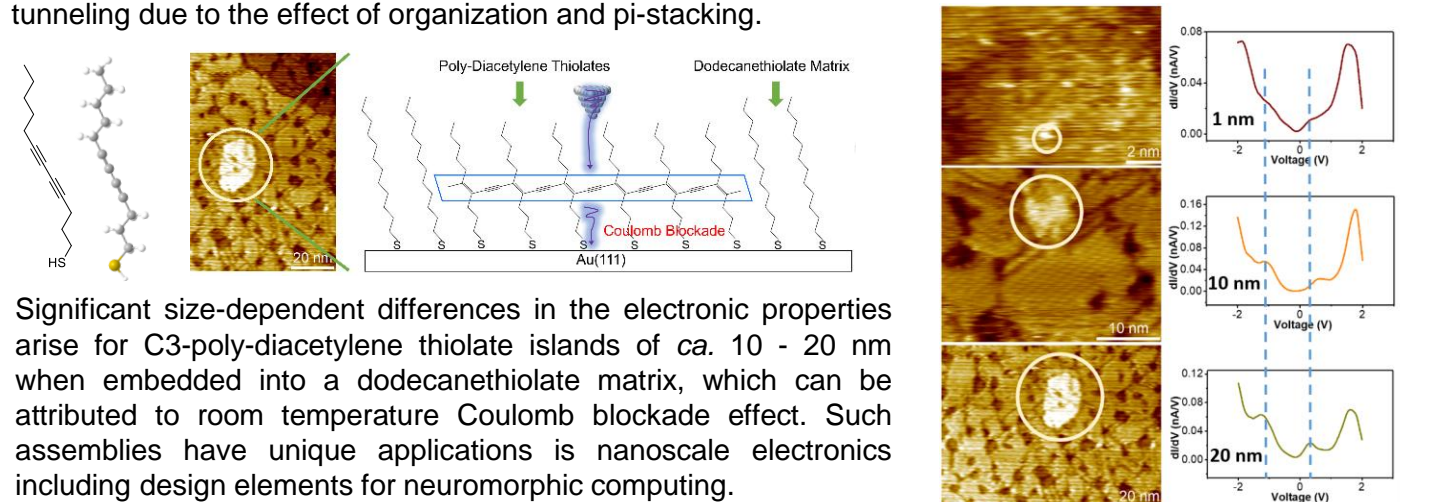
Nanoscale Materials and Devices – Top down + Bottom Up

In this work we are interested in developing approaches for the design and assembly of nanoscale materials and devices for molecular electronic, photonic and sensor applications. In our work we utilize a combination of top-down and bottom-up approaches to control and manipulate materials on the nanoscale. In much of our work we take advantage of self-organizing materials for the design of robust structures, which can be manipulated and controlled through the engineering of specific inter-molecular forces and chemical interactions with surfaces. We combine self-assembly with soft-lithographic and scanned probe lithographic techniques to enable the design of nanoscale test architectures. These include confined molecular assemblies for molecular electronics, polymer-metal heterojunctions for organic electronics and nanoscale metallic structures for plasmonic devices.

A. Tuning Charge Transport in Molecular Assemblies

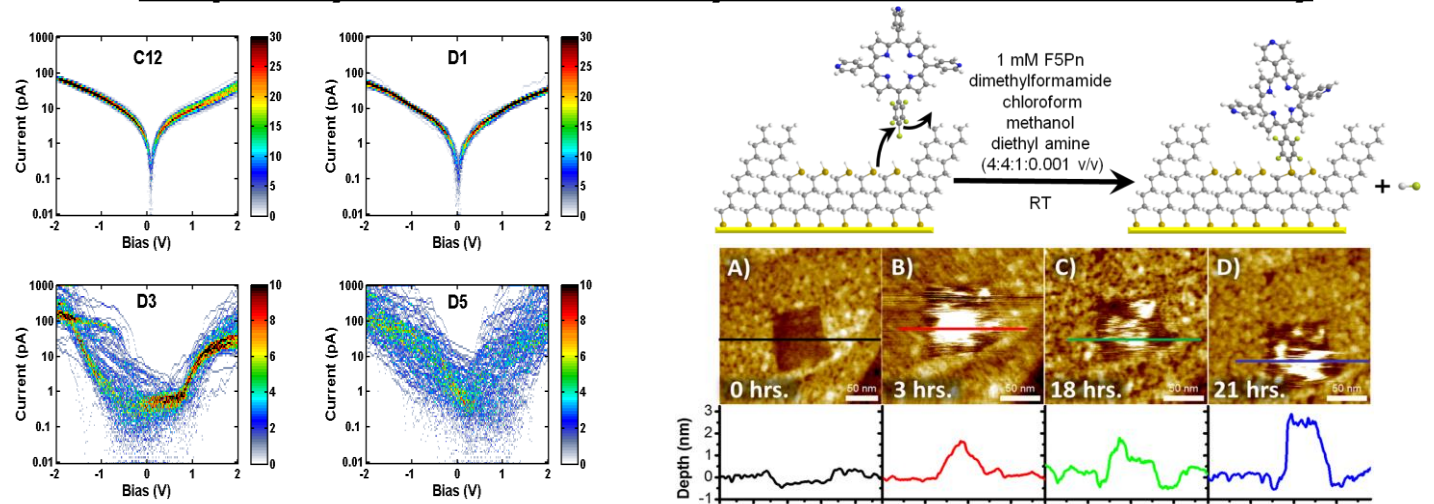


As single molecules, the electron transport in all types of porphyrin thiols investigated is similar and dominated by tunneling. However, the transport in assemblies of these porphyrin thiols departs from tunneling due to the effect of organization and pi-stacking.



F. Wu, D.K.B.N Venkata Satya, A. Brown, Z. Liu, C.M. Drain and J.D. Batteas. "Mechanical and Electronic Properties of Diacetylene and Poly-Diacetylene Self-Assembled Monolayers on Au (111)." *J. Phys. Chem. C* 124 (2020) 4081-4089.

B. Spatially Confined Chemistry to Control Molecular Assembly



Current intensity maps for neat C12 matrix (C12), ZnTPPF₄-SC₆SH clusters after one day (D1), three days (D3) and five days (D5) on a semi-log scale against the applied bias. The color scale represents the recorded counts out of 100 replicas (note the different color scale bars for top and bottom plots).

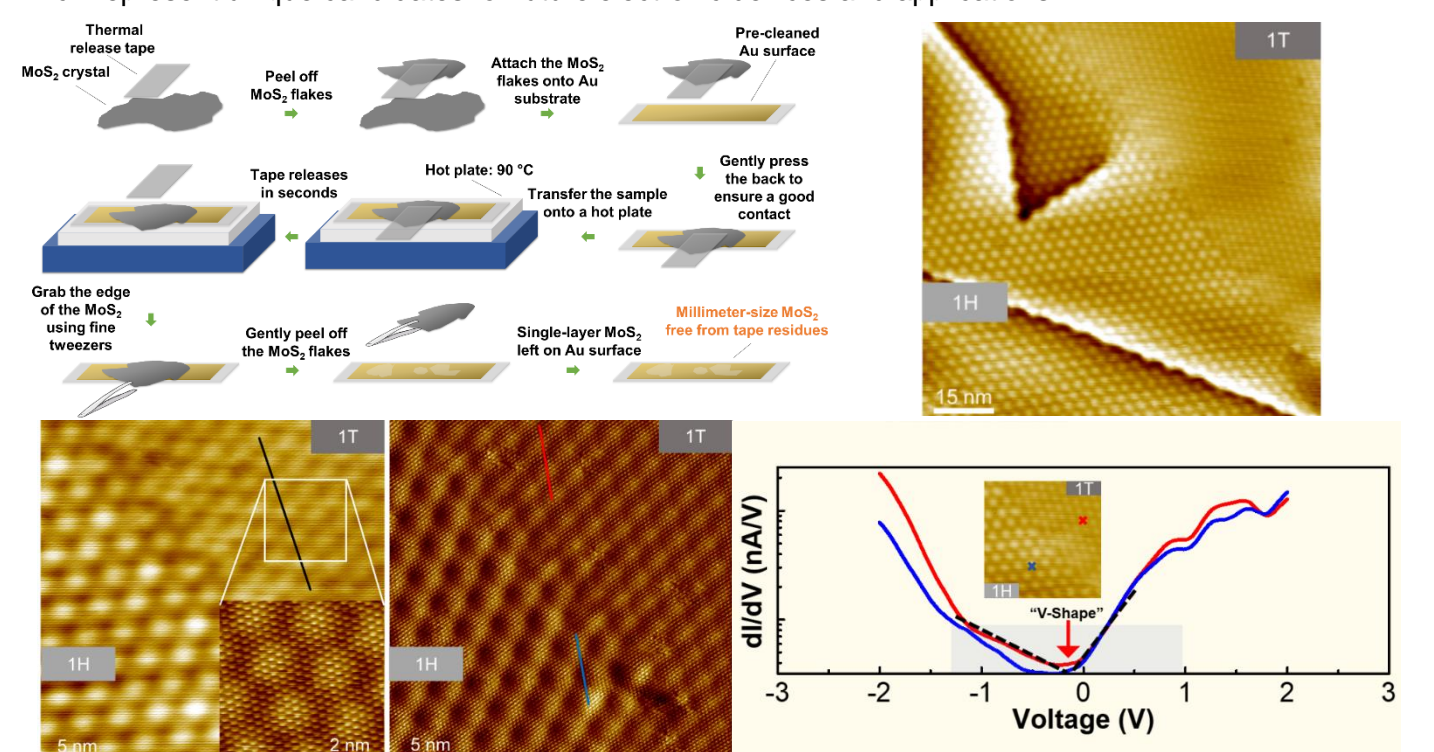
Using scanned probe lithography, surface patterns can be generated to provide templates for self-assembly to study chemistry in spatially confined geometries and to build and test nanodevices.

A. Pawlicki, E. Avery, M. Jurow, B. Ewers, A. Vilan, C.M. Drain and J.D. Batteas. "Studies of the Structure and Phase Transitions of Nano-confined Patentedithiol and its Applications in Directing Hierarchical Molecular Assemblies on Au," *J. of Physics: Cond. Matter* 28(2016), 094013.

A. Pawlicki, A. Bilan, M. Jurow, C.M. Drain and J.D. Batteas. "The Influence of Nearest-Neighbor Interactions and Assembly Dynamics on the Transport Properties of Porphyrin Supramolecular Assemblies on Au (111)," *Faraday Discussions* 204 (2017) 349-366.

C. Coherent Heterostructures in Single Layer MoS₂ on Au(111)

Single-layer heterojunctions can also be created in 2D materials. Here we report, the formation of coherent single-layer MoS₂ heterostructures, which are chemically homogenous, but show electronically distinct semiconducting (1H phase) and metallic (1T phase) domains when deposited on Au(111) by mechanical exfoliation. The exfoliation technique we developed and employed in these studies, eliminates the tape residues usually found in other exfoliation methods, and also leads to single-layer MoS₂ with millimeter size. Our work provides some intriguing guides to the production of macroscale two-dimensional heterostructures, which represent unique candidates for future electronic devices and applications.



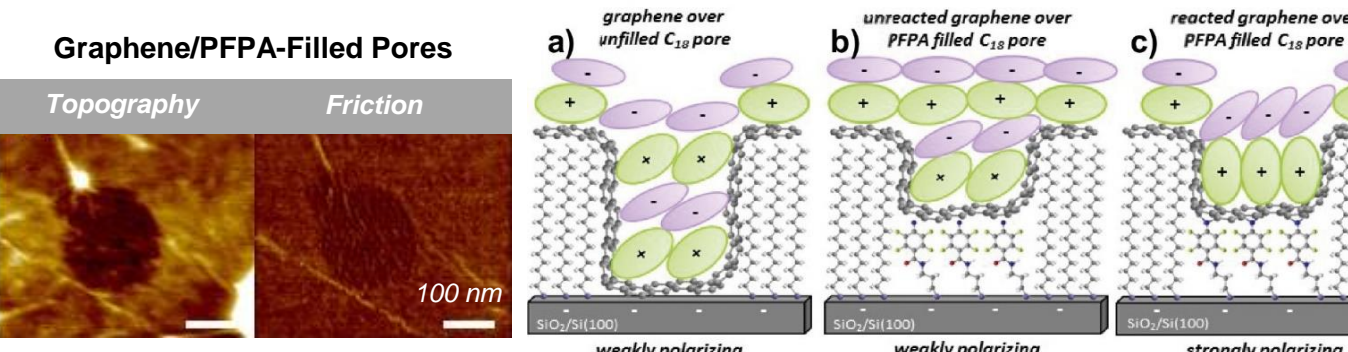
The formation and transition of the 1T-MoS₂ phase can be explained by charge transfer from the Au substrates and the built-in strain from the adhesion to the Au substrates.

F. Wu, Z. Liu, N. Hawthorne, M. Chandross, Q. Moore, N. Argibay, J. Curry and J.D. Batteas. "Formation of Coherent 1H-1T Heterostructures in Single Layer MoS₂ on Au(111)," *ACS Nano* 14 (2020) 16939-16950.

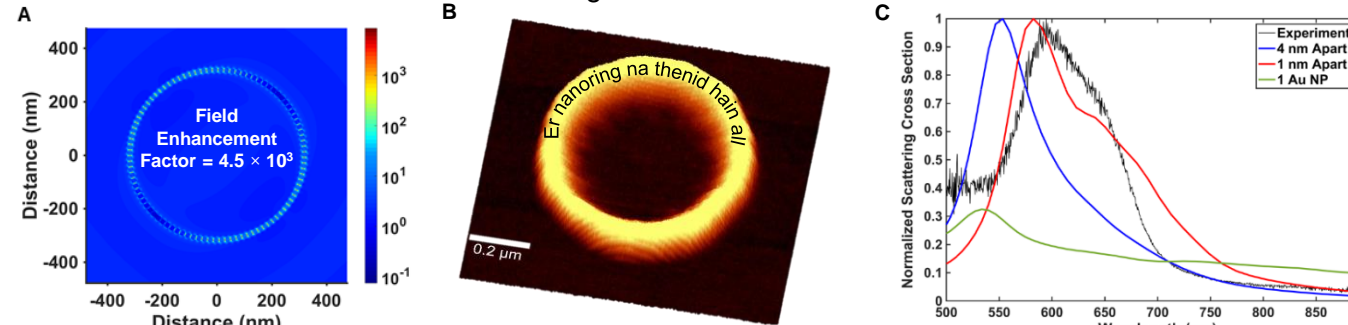
D. Architected Graphene Interfaces to Control Ionic Liquid Assembly

The deposition of graphene on surfaces with patterned arrays of silane self-assembled monolayers (SAMs) provides a facile route to tuning its optoelectronic properties. Here we use microsphere lithography to create a SAM with arrayed pores. These pores can remain empty, or, other species such as perfluorophenylazide (PFPA) can be added. Following fabrication, single layer graphene is transferred onto the patterned mixed-SAM. Heat can then be used to drive the reaction of the azide on the PFPA molecules with the graphene lattice.

A Multifunctional Graphene Structure
 The mixed-SAM/graphene heterostructure described above produces a versatile platform for studying and harnessing graphene's properties. For instance, the local pinning of graphene to the substrate prevents the out-of-plane deformations that typically dominate graphene's frictional response. Additionally, the local functionalization can be used to tailor the packing of ionic liquids (ILs) for use in capacitors. Graphene typically screens the charge of the underlying substrate providing a weakly polarizing environment for the ILs to loosely pack into the pores. After reacting with the PFPA molecules, the graphene screening in the pores is then lifted allowing the charge of the underlying substrate to influence the IL packing.



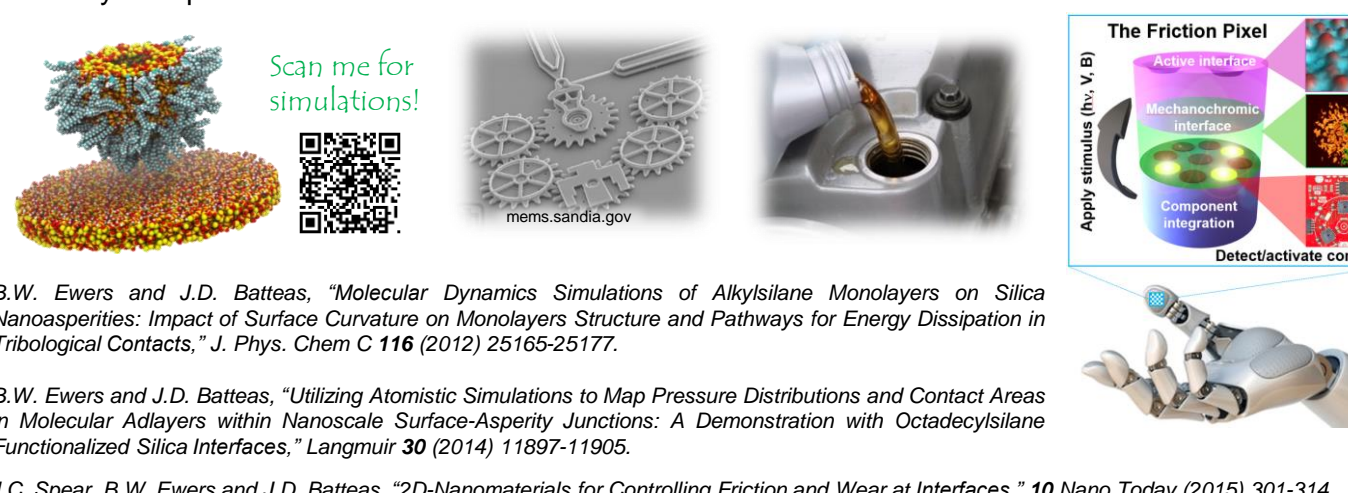
E. Tunable Plasmonic Assemblies
 Patterns of Au nanorings were fabricated using the method described above. AFM images of the nanorings were collected (B) and plasmonic coupling of the ring structure was measured experimentally by collecting dark-field scattering spectra of individual nanorings. The scattering cross section was then modeled using full-wave optical simulations revealing an inter-particle contribution to the electric field enhancement (A) in addition to the resonance also exhibited in solid ring structures. The scattering cross section peak position and shape determined a ~1nm separation between nanoparticles (C). The exhibited field-enhancement can be used to drive reactions or contribute to single-molecule detection.



A. Pravitasari, M. Negrilo, K. Light, W.-S. Chang, S. Link, M. Sheldon, and J.D. Batteas. "Using Particle Lithography to Tailor the Architecture of Au Nanoparticle Plasmonic Nanoring Arrays," *J. Phys. Chem. B* 122 (2018) 730-736.

Nanotribology – Controlling Friction

Wear and energy dissipation resulting from friction between interfaces represents an enormous cost to society, in fact it is estimated that 20% of the world's energy is lost to friction. Moreover, new and demanding applications such as Micro-electromechanical systems devices (MEMS) important for the Internet-of-Things, and space-based applications, that include systems such as satellites and rovers, as well as robotics in general, all face significant challenges from the need to control friction in both passive and active ways. Even on the largest scales (earthquakes) the fundamental nature of friction at interfaces is at play. To this end, our lab is seeking to master friction from the atomic to the tectonic by bridging these scales through a new understanding of the laws of friction on the nanoscale, and applying this to the design of new materials and approaches that can actively manipulate and control friction.



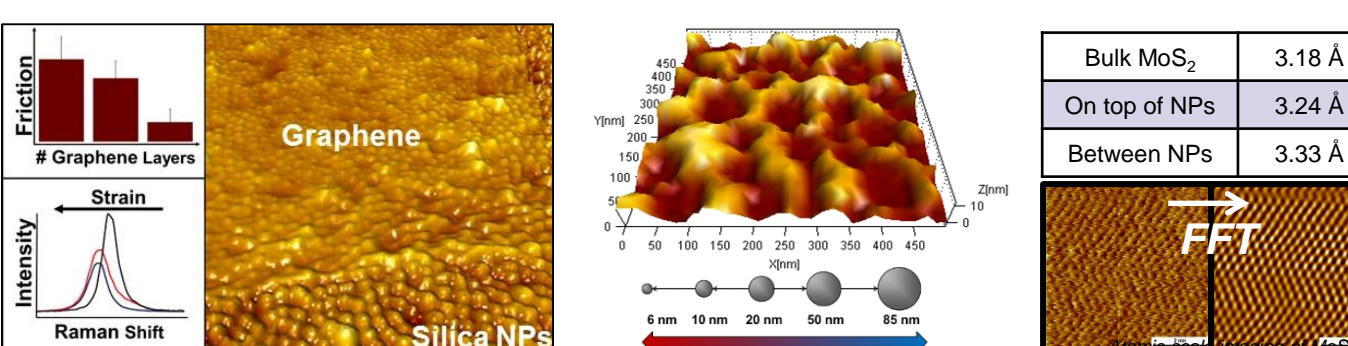
B.W. Ewers and J.D. Batteas. "Molecular Dynamics Simulations of Alkylsilane Monolayers on Silica Nanoparticles: Impact of Surface Curvature on Monolayers Structure and Pathways for Energy Dissipation in Tribological Contacts," *J. Phys. Chem. C* 116 (2012) 25165-25177.

B.W. Ewers and J.D. Batteas. "Utilizing Atomistic Simulations to Map Pressure Distributions and Contact Areas in Molecular Adlayers within Nanoscale Surface-Asperity Junctions: A Demonstration with Octadecylsilane Functionalized Silica Interfaces," *Langmuir* 30 (2014) 11897-11905.

J.C. Spear, B.W. Ewers and J.D. Batteas. "2D-Nanomaterials for Controlling Friction and Wear at Interfaces," *10 Nano Today* (2015) 301-314.

A. 2D Materials as Active Coatings for Controlling Friction

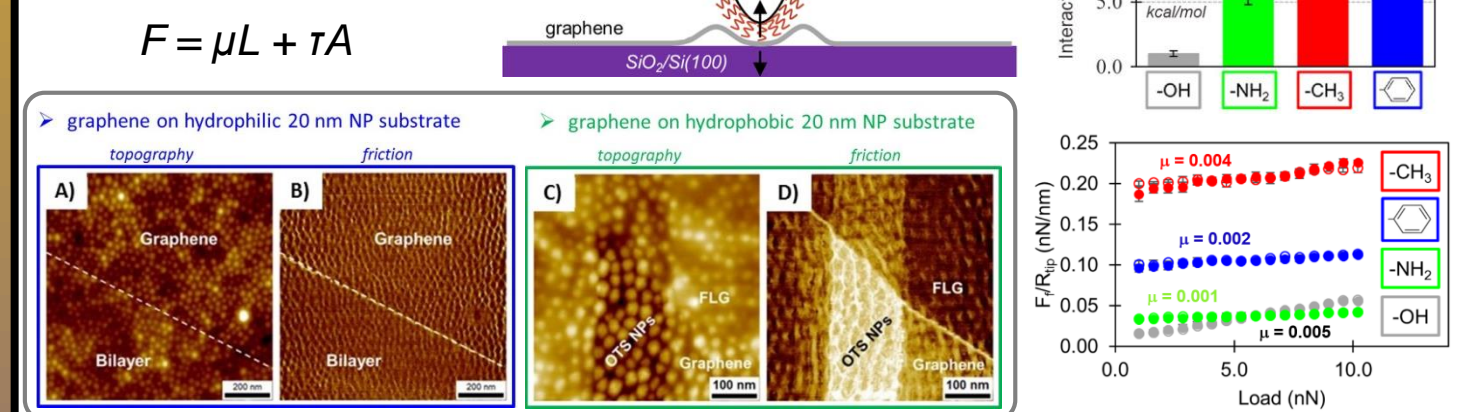
On real surfaces (with nm scale roughness), both graphene and MoS₂ exhibit dynamic frictional properties.



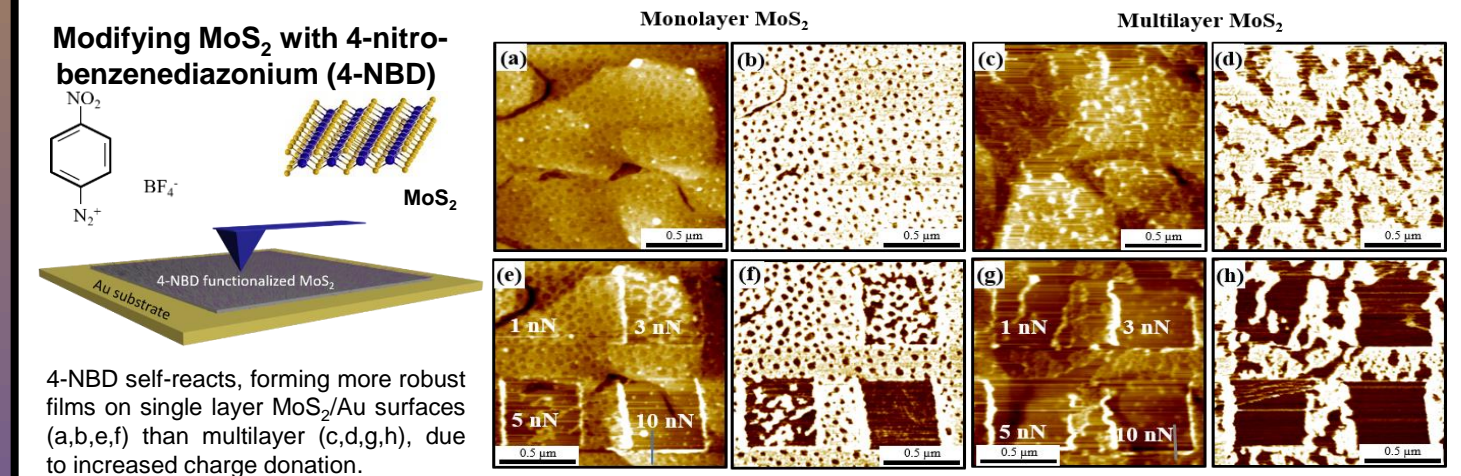
J.C. Spear, J.P. Custer and J.D. Batteas. "The Influence of Nanoscale Roughness and Substrate Chemistry on the Frictional Properties of Single and Few Layer Graphene," *Nanoscale* 7 (2015) 10021-10029.

M.B. Elinski, Z. Liu, J.C. Spear and J.D. Batteas. "2D or not 2D? The Impact of Nanoscale Roughness and Substrate Interactions on the Tribological Properties of Graphene and MoS₂," *J. of Phys. D: Appl. Phys.* 50 (2017)103003.

The dynamic tribological response of graphene can be modulated by tuning the surface chemistry of both the top sliding contact and supporting substrate.



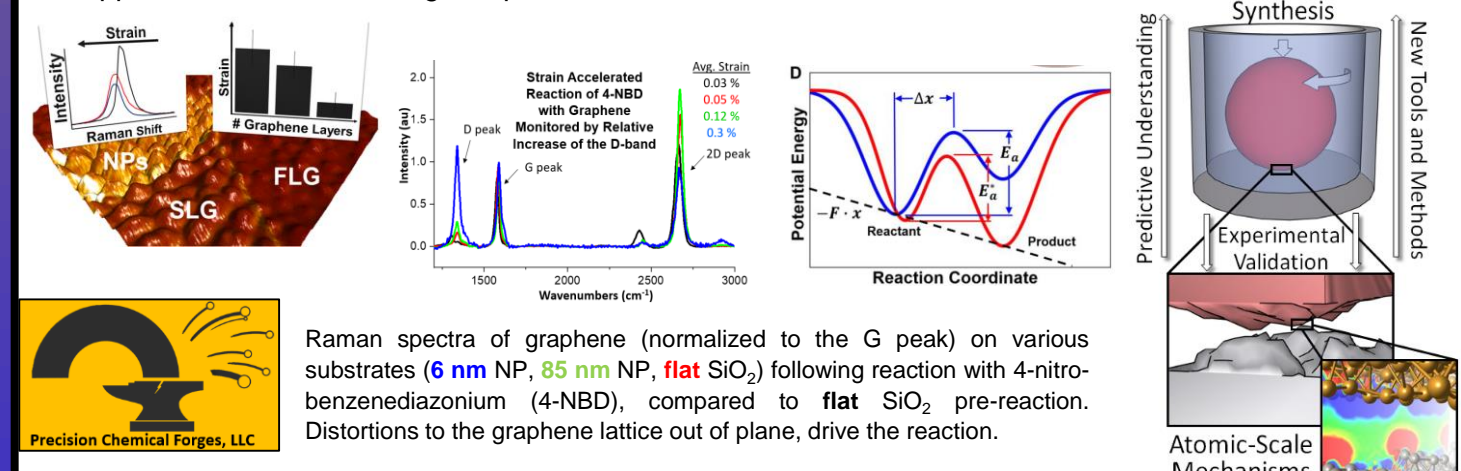
Elinski, M. B.; Menard, B. D.; Liu, Z.; Batteas, J. D. "Adhesion and Friction at Graphene/Self-Assembled Monolayer Interfaces Investigated by Atomic Force Microscopy," *J. Phys. Chem. C* 121 (2017) 5635-5641.



4-NBD self-reacts, forming more robust films on single layer MoS₂/Au surfaces (a,b,e,f) than multilayer (c,d,g,h), due to increased charge donation.

B. Mechanochemistry

Our newly funded NSF Center for the Mechanical Control of Chemistry (CMCC) focuses on developing a fundamental understanding of mechanically driven chemical reactions, which is important for not only combating wear in sliding contacts, but in advancing green methods for chemical synthesis. The application of mechanical force acts to drive chemical reactions along new reaction paths in response to the applied force vectors acting on specific reaction coordinates.



Raman spectra of graphenes (normalized to the G peak) on various substrates (6 nm NP, 85 nm NP, flat SiO₂) following reaction with 4-nitrobenzenediazonium (4-NBD), compared to flat SiO₂ pre-reaction. Distortions to the graphene lattice out of plane, drive the reaction.

C. Friction in Geologic Faults: From Atomic to Tectonic

Here we seek to obtain fundamental physical insights into the processes underlying friction in seismicogenic materials, with the goal of replacing empirical 'rate and state' (RSF) friction laws, which underpin earthquake models, with key descriptors that will create a more predictive foundation. This project involves closely-coordinated experiments and simulations that integrate knowledge and approaches in geophysics with physics, materials science, chemistry and mechanics, with initial investigations of mechanical and chemical mechanisms of friction down to the atomic scale, and will extend our work for the first time beyond silica and quartz to other minerals.

Adapted from: NSF report on Modeling Earthquake Source Processes: From Tectonics to Dynamic Rupture (last access 01/23/2020) <http://www.seismolab.caltech.edu/modeling-earthquake-source-workshop.html>

J.M. Holt and J.D. Batteas. "Wear of Mica in Aqueous Solutions: Direct Observation of Defect Nucleation by AFM," *Langmuir* 21 (2005) 633-639.

Education and Outreach

Education and outreach activities in our group have focused on teaching the general public about nanoscience and nanotechnology through our Chemistry Open House which is part of Texas A&M's Engineering and Science Day held in October of each year. We have also integrated our labs research into the physical chemistry labs at TAMU, and have developed a Nanotechnology course as part of Texas A&M's summer Youth Adventure Program!

B.W. Ewers, A.E. Schuckman and J.D. Batteas. "Why Did the Electron Cross the Road? A Scanning Tunneling Microscopy (STM) Study of Molecular Conductance for the Physical Chemistry Lab," *J. Chem. Educ.* 91 (2014) 283-290.

Acknowledgements

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