Modulation of the Electronic Structure and Chemical Reactivity of 2D Materials by the Application of Strain

Quentarius Moore

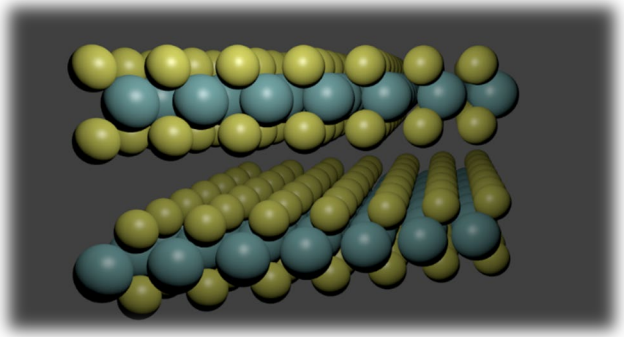
Advisor: James D. Batteas

DOE CSGF Program Review

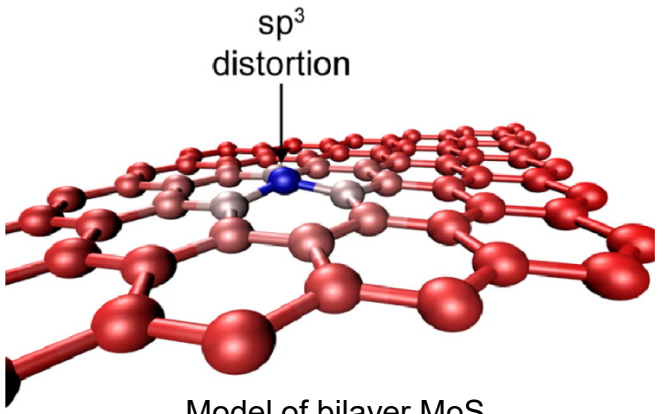
4th Year Fellow Presentation

Outline

- Introduction
  - Motivation and Challenges
  - Mechanochemistry
- Research Components
  - Modulating the Chemical Reactivity of Graphene with Aryl Diazonium by Application of Strain
  - Tuning the Electronic and Chemical Properties of Strained MoS_2 under Reactive Species (oxygen radical, O_2 and H_2O)
- Summary and Acknowledgements

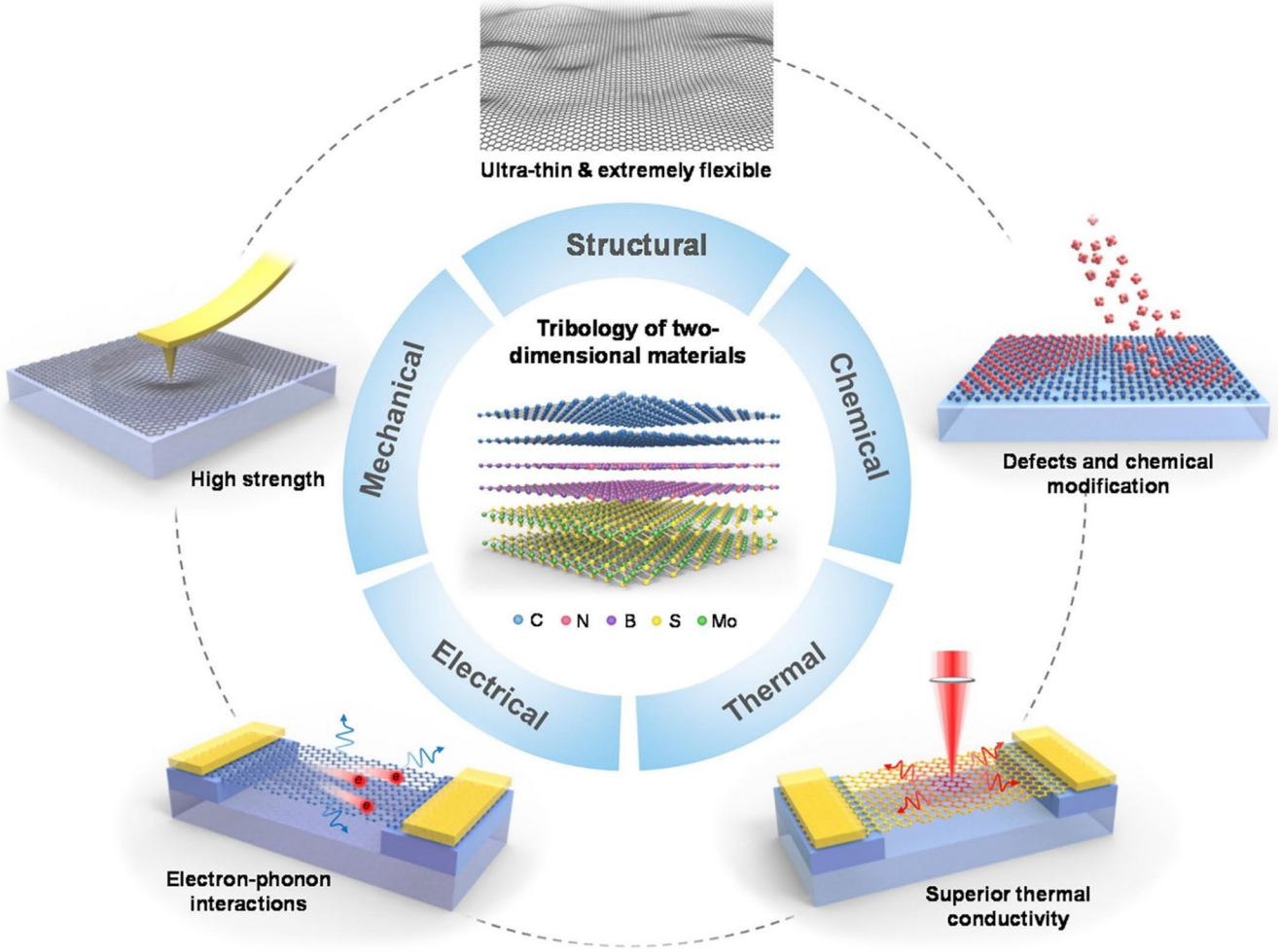


Model of bilayer MoS_2



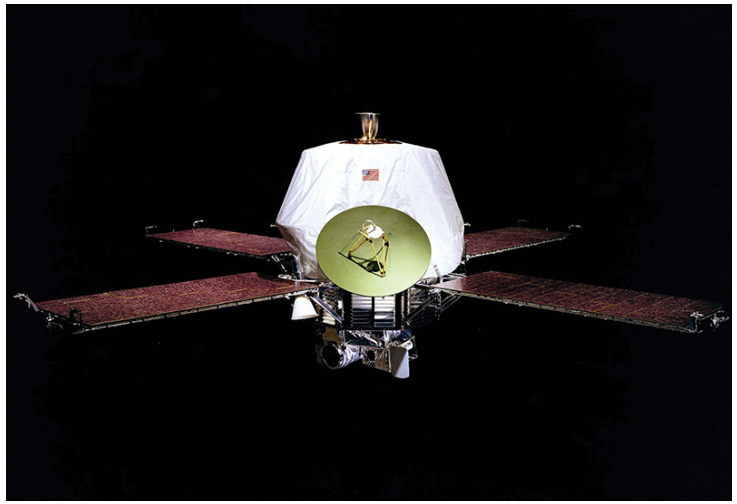
Model of bilayer MoS_2

Two-Dimensional (2D) Materials



Overview of structural, mechanical, electrical, thermal, and chemical properties of 2D materials that are relevant to tribological performance

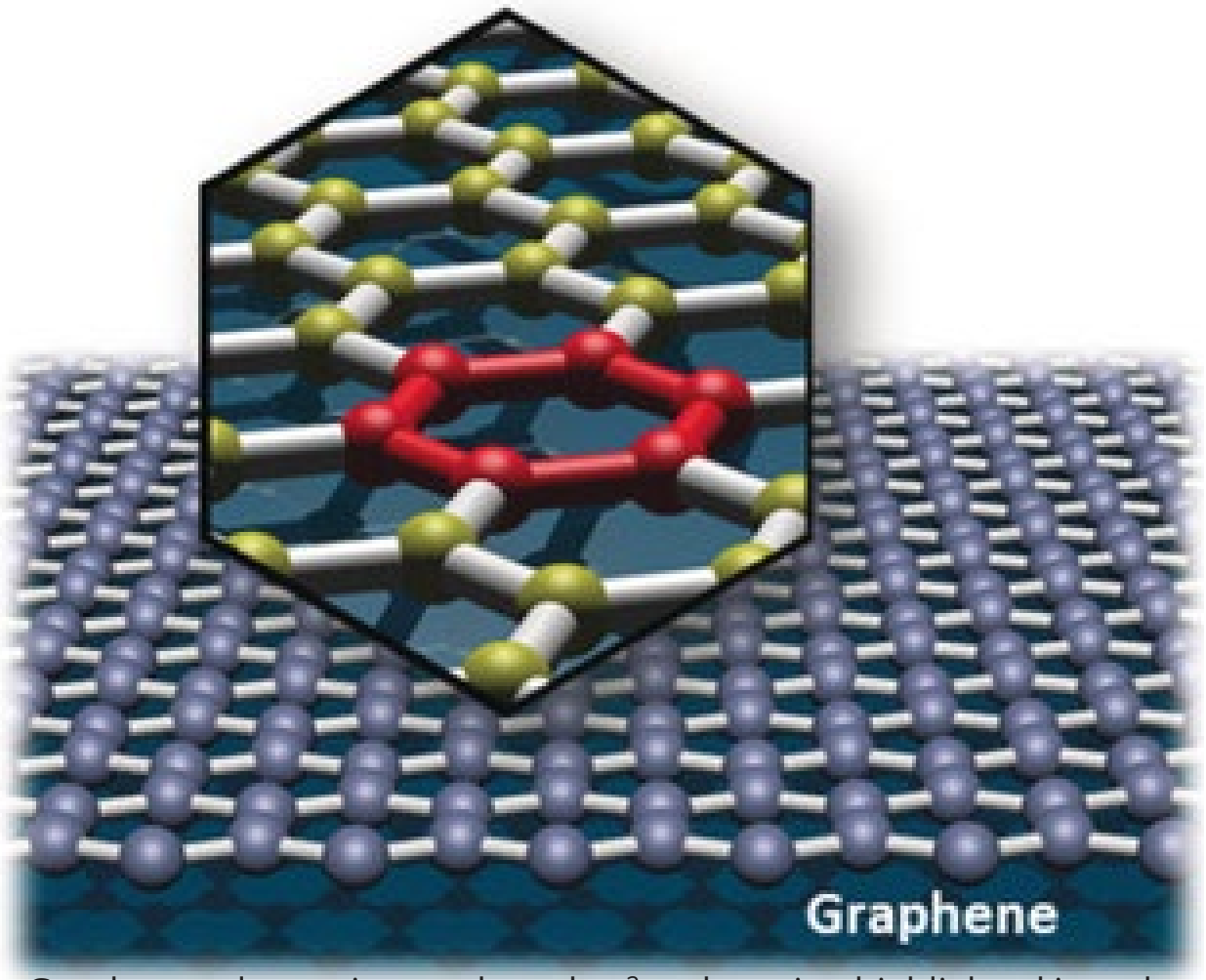
- 2D & Atomically Thin
- Exceptional mechanical and frictional properties
- Flexible electronics



- Solid dry lubricant
- Anti-wear performance

- Zhang, S; et al. *Tribology of two-dimensional materials: From mechanisms to modulating strategies*. Mater. Today. **2019**, 26, 67-86
- NASA Dry Lubricant Smooths the Way for Space Travel, Industry https://spinoff.nasa.gov/Spinoff2015/ip_7.html **2015**

Graphene



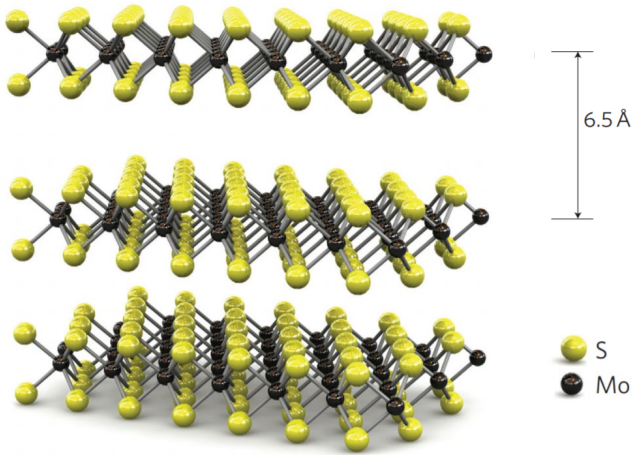
Graphene: planar six membered sp^2 carbon ring highlighted in red

- Exceptional flexibility and mechanical strength
- Network of conjugated pi-system
- Application as solid lubricant, sensor, and optoelectronics

- Hirsch, A.; Hauke, F., *Post-Graphene 2D Chemistry: The Emerging Field of Molybdenum Disulfide and Black Phosphorus Functionalization*. Angew. Che. Int. **2017**, 57, 4338-4354

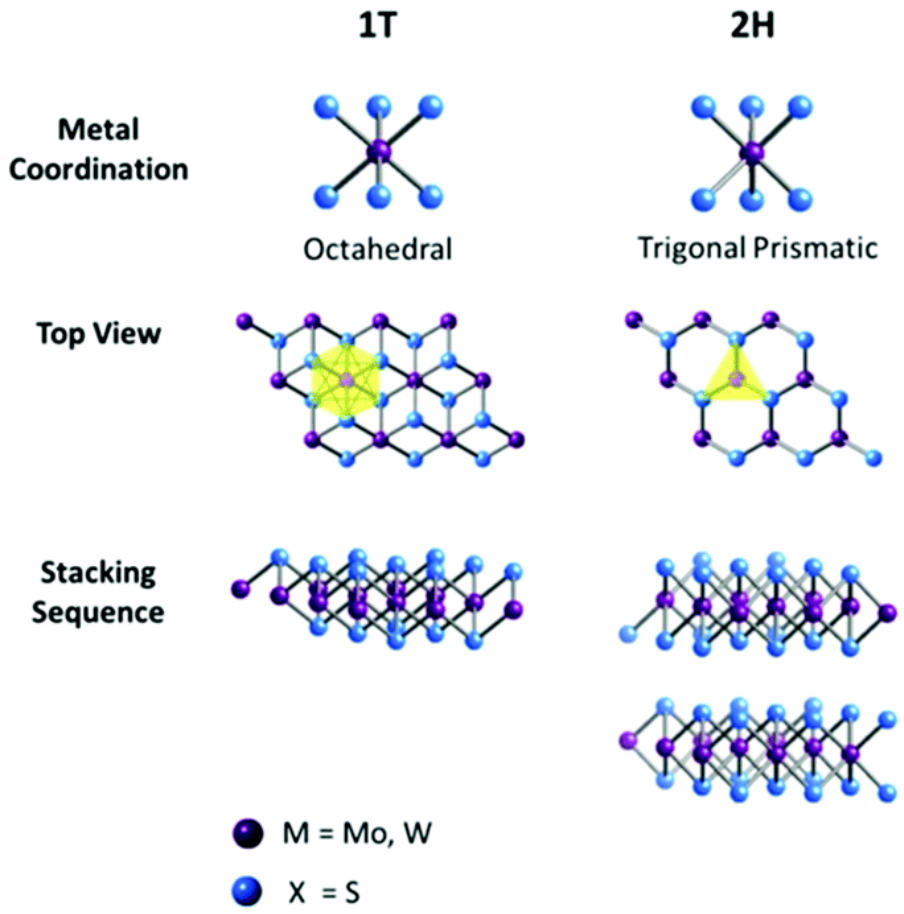
2D Transition Metal Dichalcogenides

Molybdenum disulfide (MoS_2)



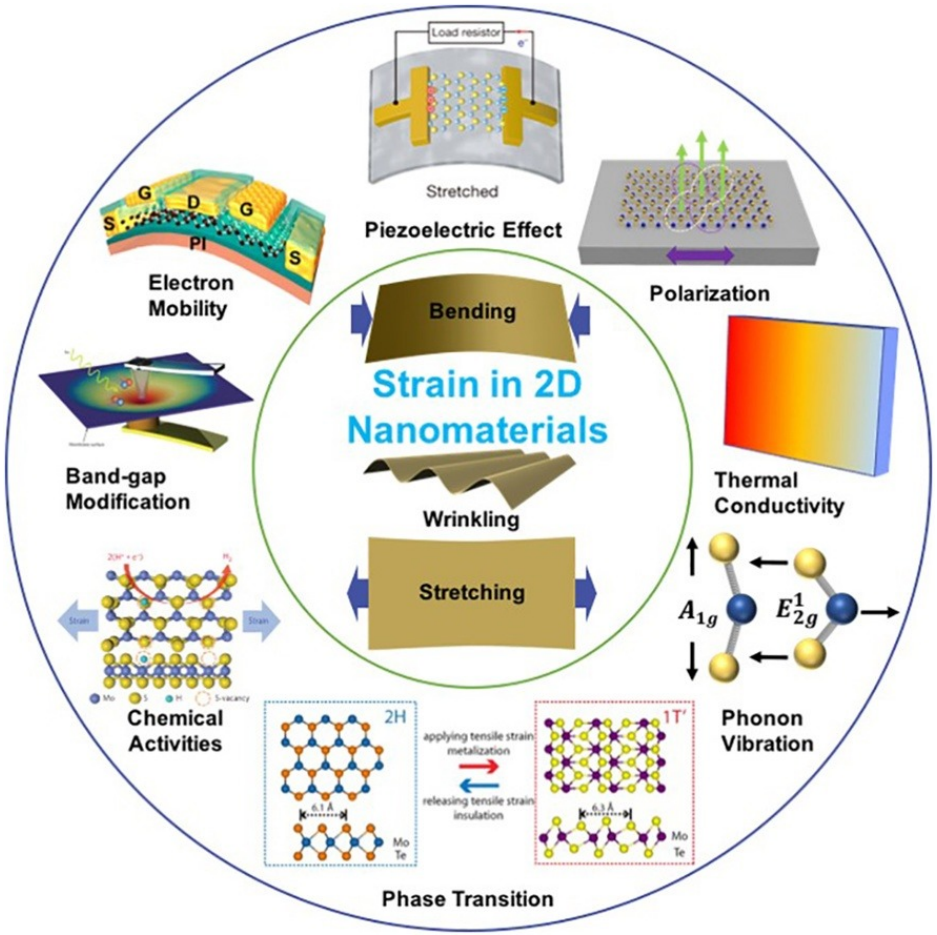
- Exciting mechanical, electronic and frictional properties
- Promising potentials for solid lubricants, ion batteries, low power transistors, optoelectronic devices

- Stable against reactions with environmental species
- Three atomic layers hexagonal



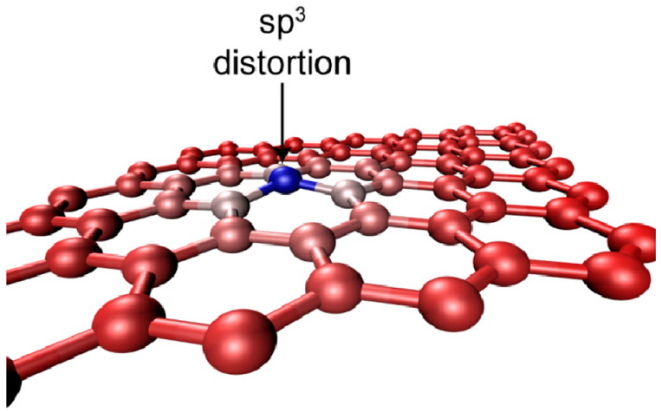
- Toh, R.; Pumera, M., et al. *3R phase of MoS_2 and WS_2 outperforms the corresponding 2H phase for hydrogen evolution*. Chem. Commun. **2017**, 53, 3054-3057
- Radisavljevic,B., et al. *Single-layer MoS_2 Transistors*. Nature Nanotechnology **2011**, 6, pages147–150

Challenges of 2D Material Chemistry



- Tunable electronic and optical properties

- Inert basal plane
- Difficult to initiate and control degree of functionalization
- Non-uniform coverage

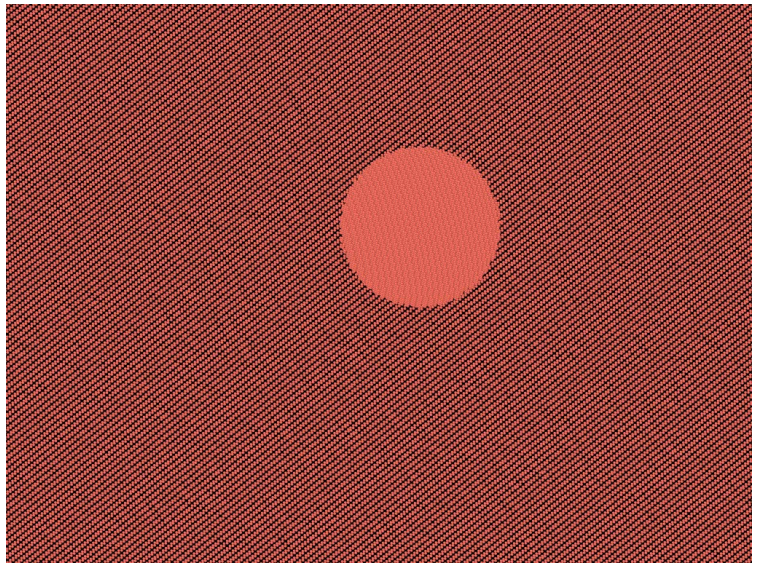


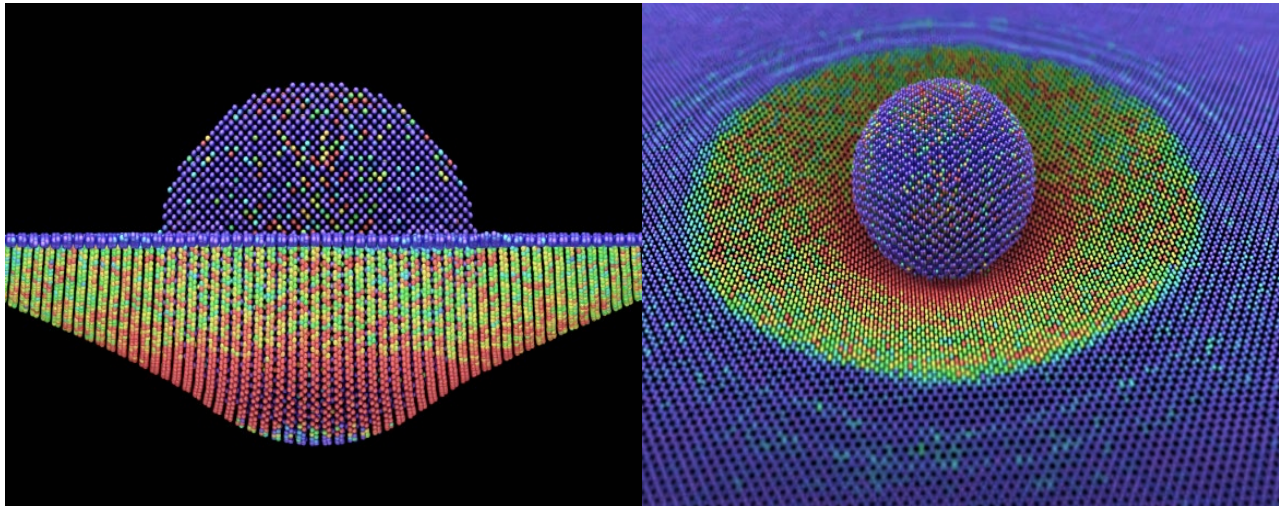
- Typical lattice distortion resulting from a single covalent adsorbate on graphene.

- Hirsch, A.; Hauke, F., *Post-Graphene 2D Chemistry: The Emerging Field of Molybdenum Disulfide and Black Phosphorus Functionalization*. Angew. Che. Int. **2017**, 57, 4338-4354
- *Johns,J; Hersam, M. Atomic Covalent Functionalization of Graphere* Acc. Chem. Res. **2013**, 46, 1, 77–86

Goal of the overarching research projects

The fundamental understanding of how force alters reaction energies and pathways – *mechanochemistry* – is far less developed and is one of *the last fundamental frontiers in chemistry.*





Snapshot of a molecular dynamics indentation simulation, a 6 nm diamond particle (central sphere) is indenting a graphene sheet. (range: -1×10^7 bar* Å^3 to 1×10^7 bar* Å^3).

The chemical reactivity of the basal plane of 2D materials can be modulated by electronic and geometric effects through directed forces

CSGF Sponsored Research

Goal of Work: To develop a fundamental understanding of mechanochemical reactions, here we focused on how the precise application of force, and importantly, its direction, can drive chemical bond formation.

Main Projects:

1. How does varying mechanical strain of the graphene lattice affect the reactivity of graphene?

2. How does controlled strain influence the reactivity of MoS_2 on metal substrates?

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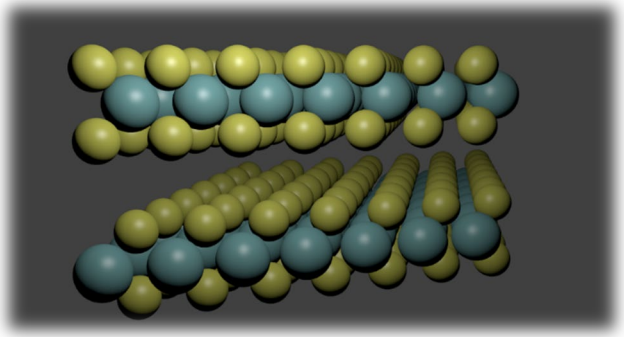
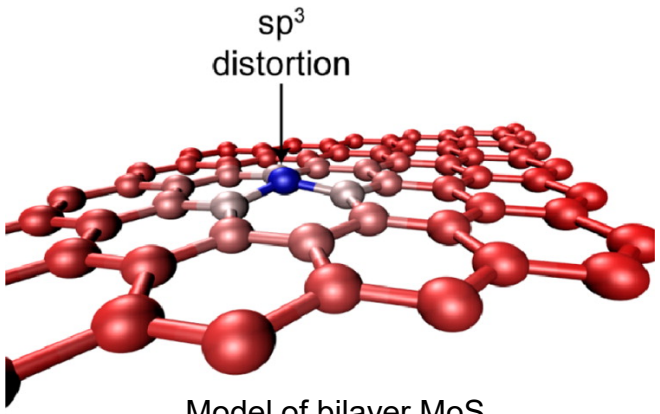


Model of bilayer MoS_2

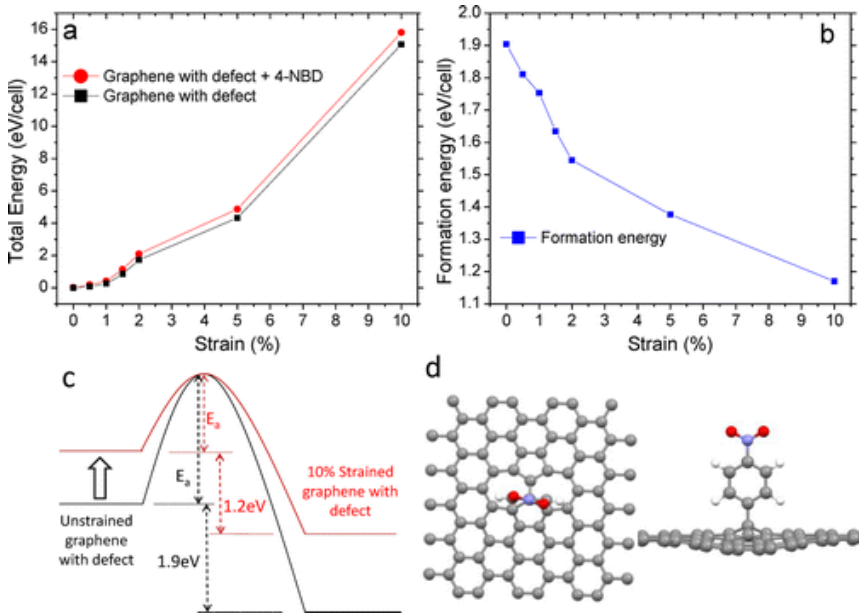


Model of bilayer MoS_2

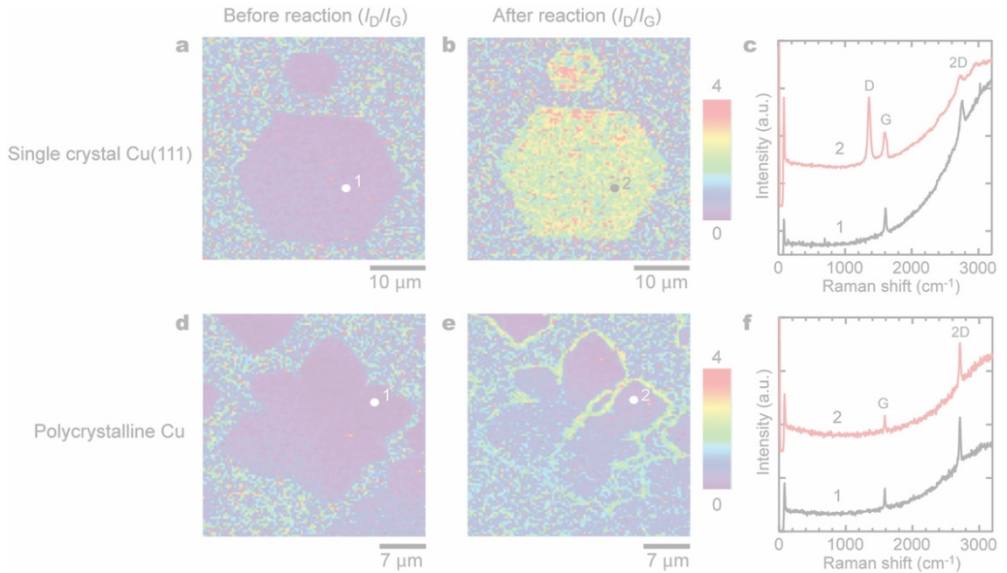
Modulating Reactivity of Graphene by Application of Strain

Q1: How does varying mechanical strain of the graphene lattice affect the reactivity of graphene?

- Tensile Strain



- Compressive Strain



- Formation energy decreases as strain increases
- Compressive strains results in enhanced reactivity

- *Bissett, M.; et al. Enhanced Chemical Reactivity of Graphene Induced by Mechanical Strain. ACS Nano.* **2013,** *7*, 10335-10343
- Li, B.; et al., *Orientation-Dependent Strain Relaxation and Chemical Functionalization of Graphene on a Cu(111) Foil.* Adv. Mater. **2018**, 30, 1706504

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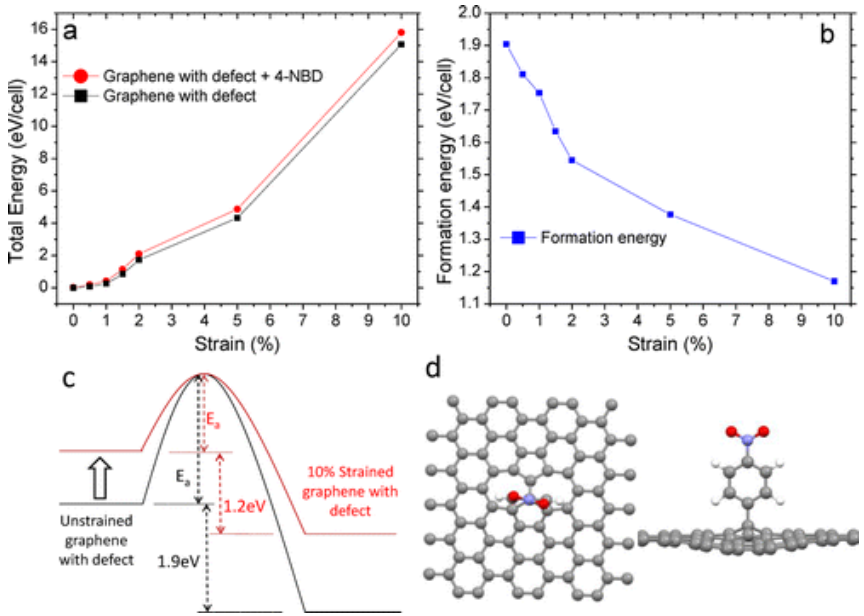

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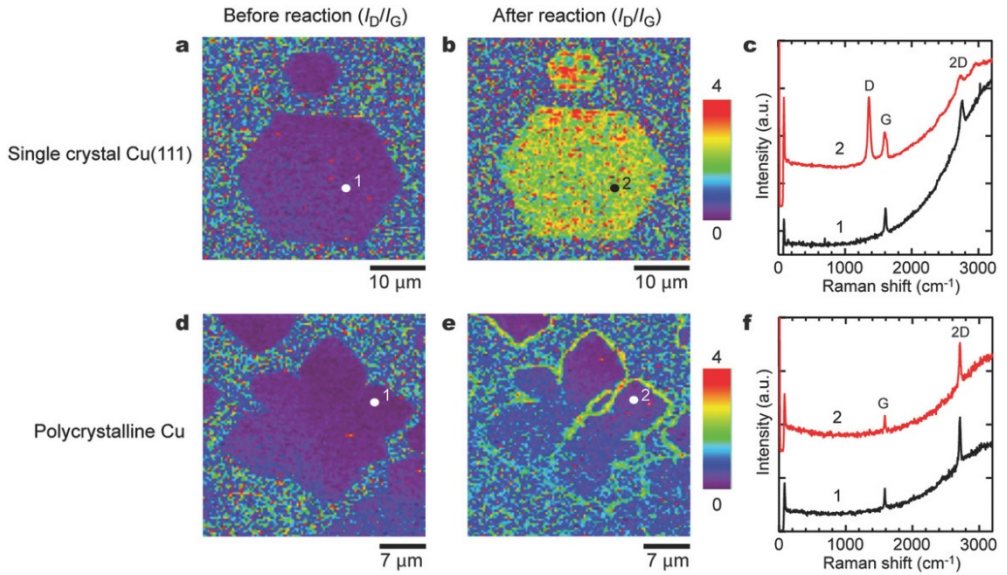

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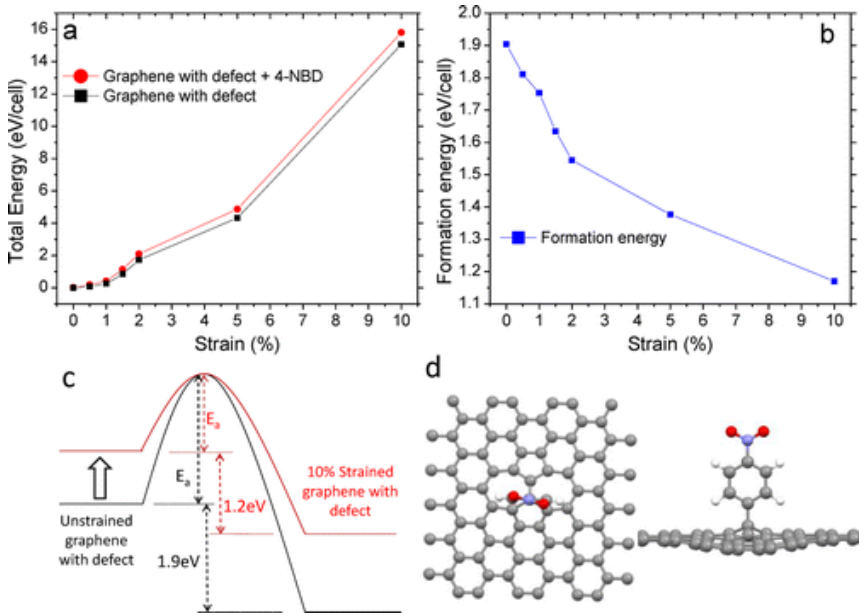

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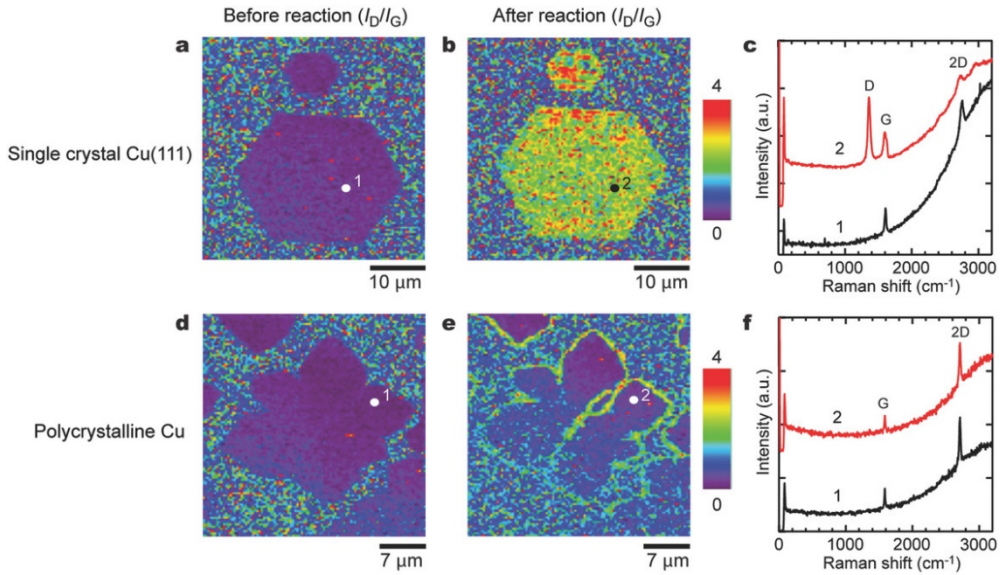

- Formation energy decreases as strain increases
- Compressive strains results in enhanced reactivity

- **Lack of systematic control of strain**
- **Difficulty determining "real" strain**
- **Decouple substrate effects from strain/reactivity experiments**

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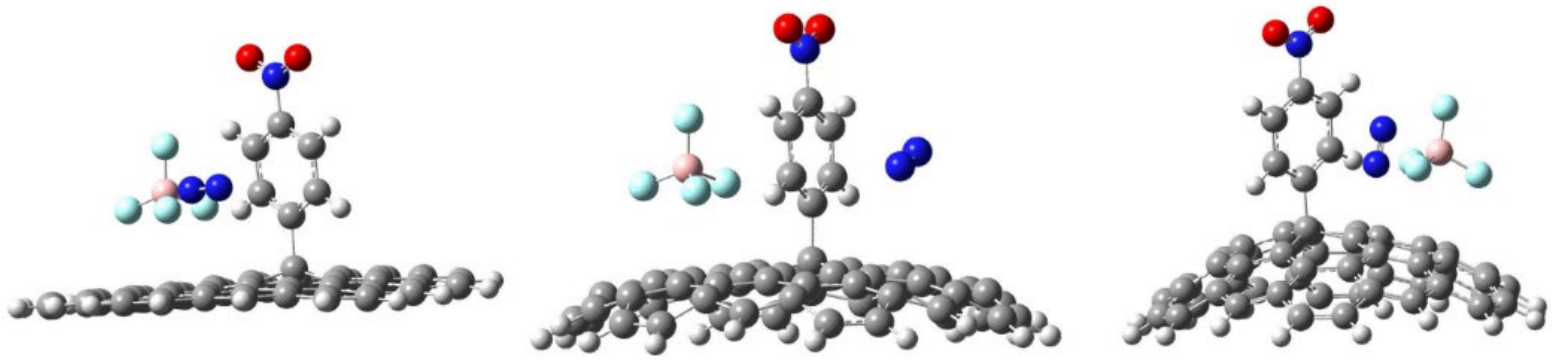
Out-of-plane strain

Radical reaction of 4-nitro-benzenediazonium tetrafluoroborate (4-NBD) with graphene



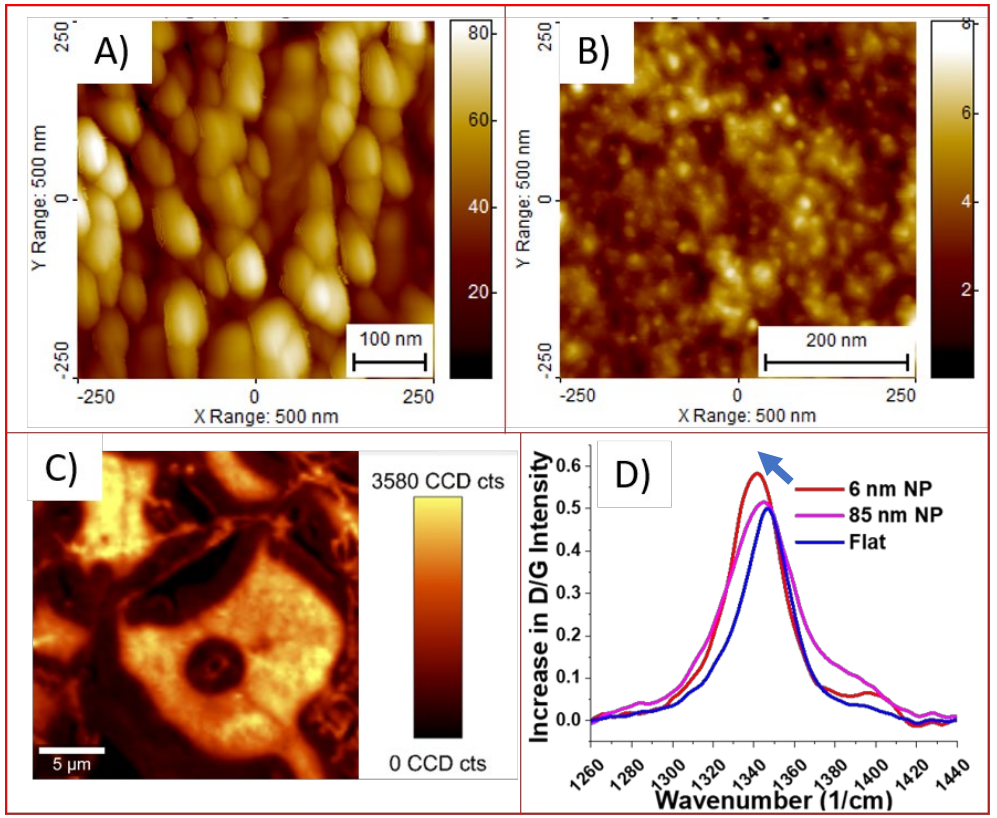
Flat 85 nm 6 nm

- We focused on how the application of force, and importantly, its direction, can drive chemical bond formation.

Experimental Findings

- Experimentally determined that an increase in curvature of the graphene lattice, leads to an increase of reactivity of graphene
- Graphene on the smaller NPs reacted to a greater extent than graphene on both the larger NPs, and on flat silica

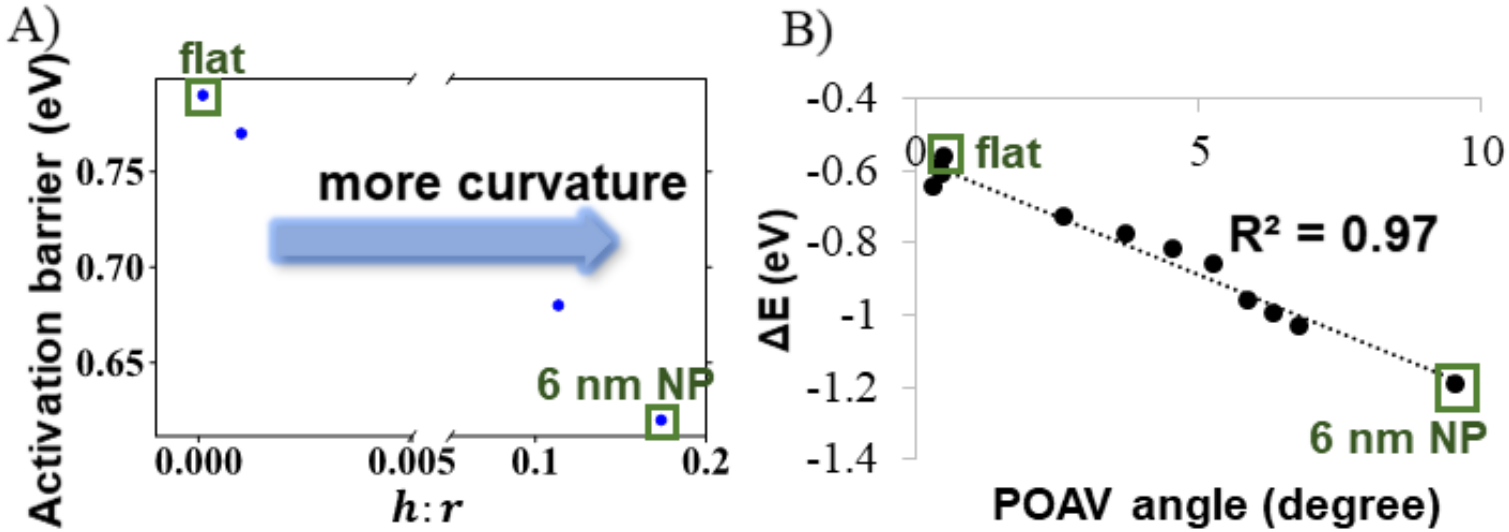
Radical reaction of 4-nitro-benzenediazonium tetrafluoroborate (4-NBD) with graphene



Representative AFM topography images of graphene-covered nanoparticle films on (A) 85 nm NP, and (B) 6 nm NP. (C) Raman D peak intensity map of graphene on 6 nm NPs after reacting with 4-NBD. (D) Comparison of D/G growth after reacting graphene on the different films.

Computational Findings

- An increase in curvature of the graphene leads to a decreased in-plane electron delocalization, lowering the activation barrier for functionalization with 4-NBD



A) Curvature-dependent activation barrier of 4-NBD functionalization. B) Correlation of the π-orbital axis vector (POAV) angle with the reaction energy (ΔE).

Key Findings

- *An increase in curvature of the graphene lattice, leads to an increase of reactivity of graphene*

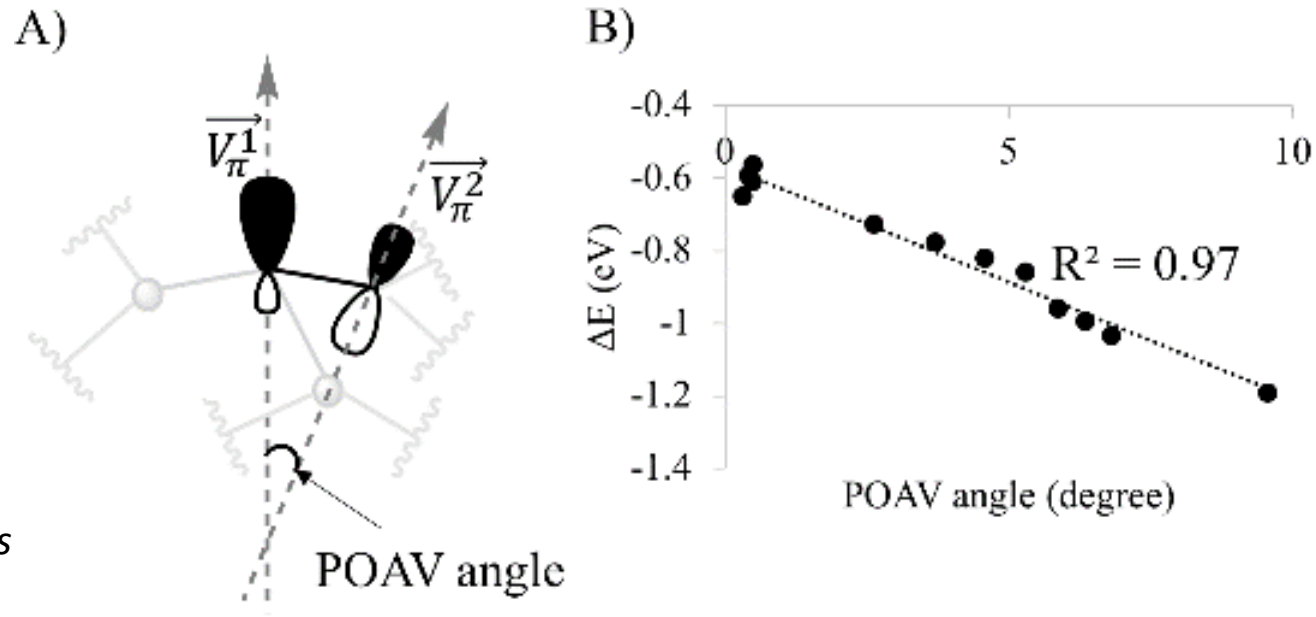


Fig. Z. A) Schematic diagram showing the relative orienation of graphene frontier orbitals. B) Correlation of the POAV angle with the reaction energy (***Δ***E).

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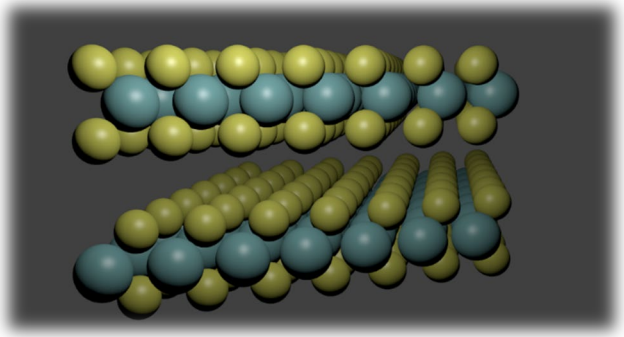
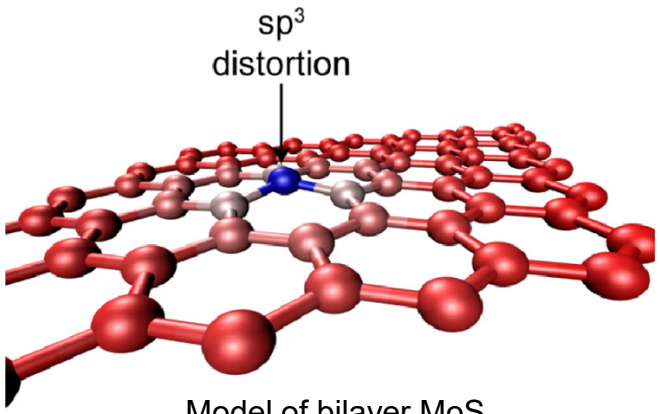


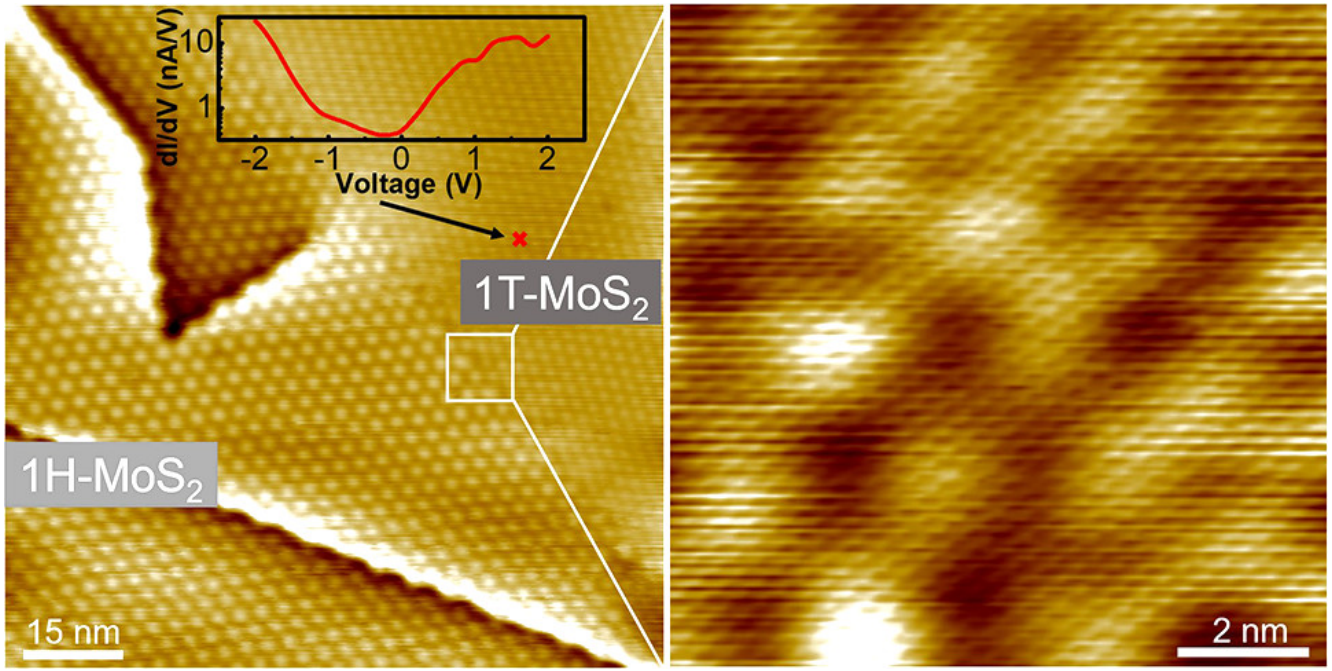
Model of bilayer MoS_2



Model of bilayer MoS_2

Modulating Properties of Strained MoS_2

- We see the formation of coherent single-layer 1H-1T MoS_2 heterostructures by mechanical exfoliation on Au(111)

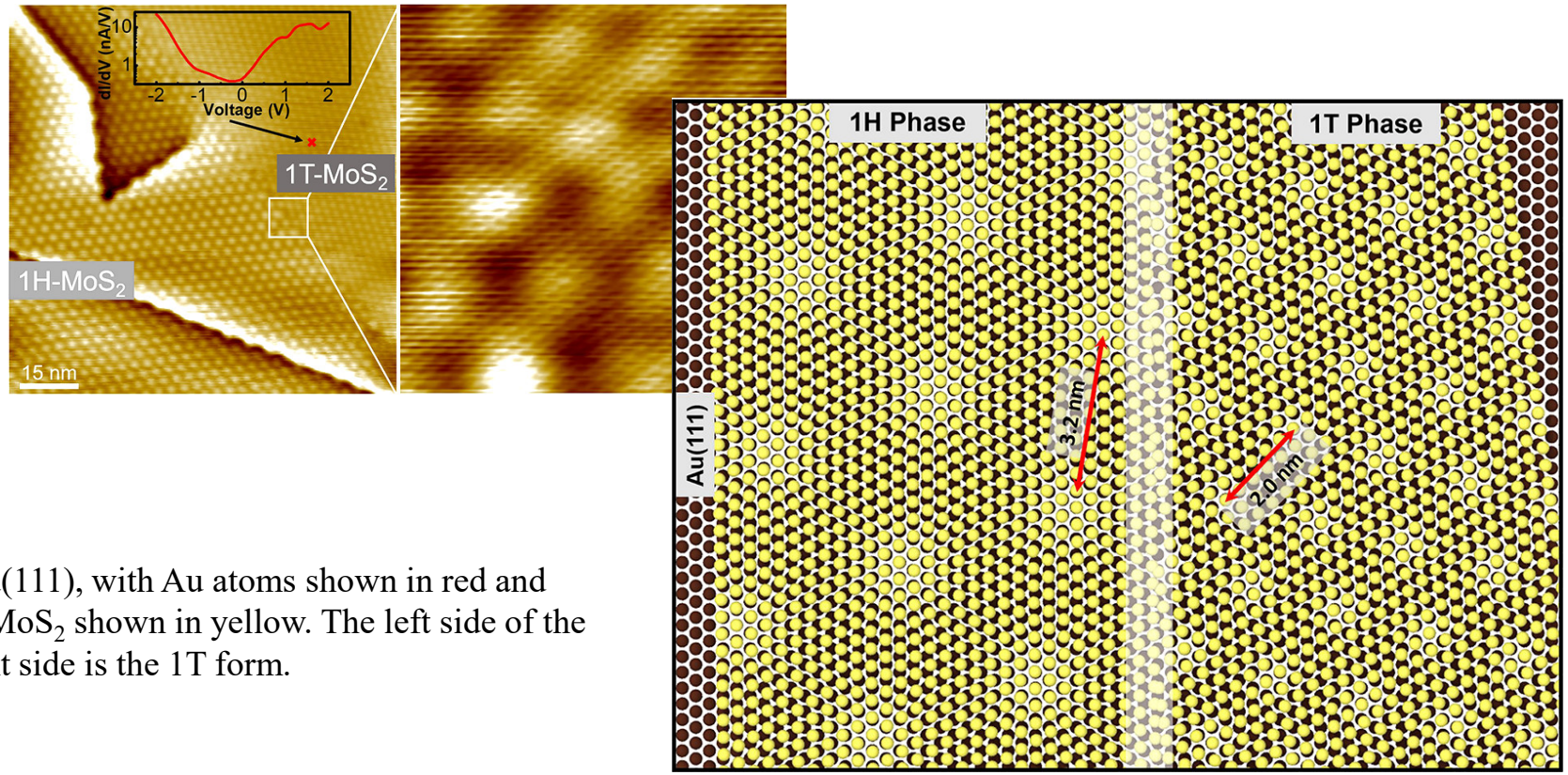


Large-scale STM image (V_{bias} = +500 mV, I_t = 0.5 nA) of single-layer MoS_2 with two different moiré patterns

➢ *Wu, F.; et al. Formation of Coherent 1H–1T Heterostructures in Single-Layer MoS2 on Au(111) ACS Nano.* **2020,** *14*, 12, 16939-16950

Formation of Coherent MoS_2 Heterostructures

Modulating Properties of Strained MoS_2



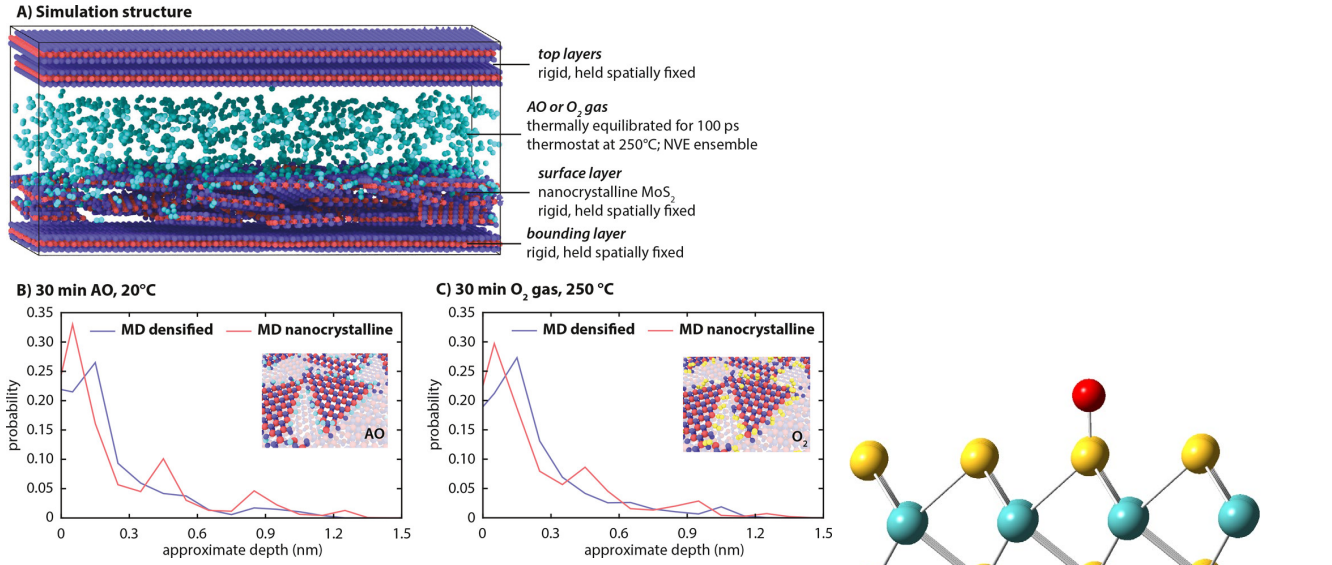
Simulated moiré patterns for MoS_2 on Au(111), with Au atoms shown in red and sulfur atoms from the lower layer of the MoS_2 shown in yellow. The left side of the MoS_2 flake is the 1H form, while the right side is the 1T form.

Reactivity of MoS_2 in the Presence of Reactive Species

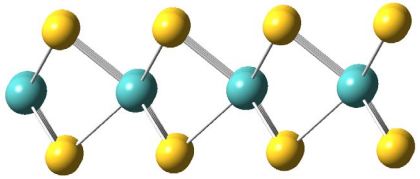
Oxidation of Strained MoS_2

How is the initial step of oxidation affected by:

- Layer thickness
- Metal substrate
- Strain



(A) Structure of MD simulation using a reactive force field (ReaxFF) for the interaction between MoS_2 and AO and O_2 gas.



Model of oxygen radical reacted to the surface of bi-layer MoS_2

Goal: assessing the reactivity of MoS_2 in the presence of reactive species (i.e. oxygen radical, O_2, H_2O, etc.)

- *Q. Moore, N.S. Bobbitt and M. Chandross, The effects of oxidation on friction in MoS2,* ***in preparation****.*
- *Curry, J., et al, Impact of Microstructure on MoS2 Oxidation and Friction,* ***ACS Appl. Mater. Interfaces 2017, 9, 33, 28019–28026****.*

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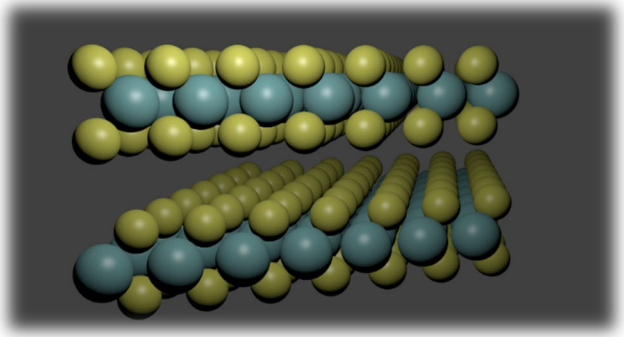

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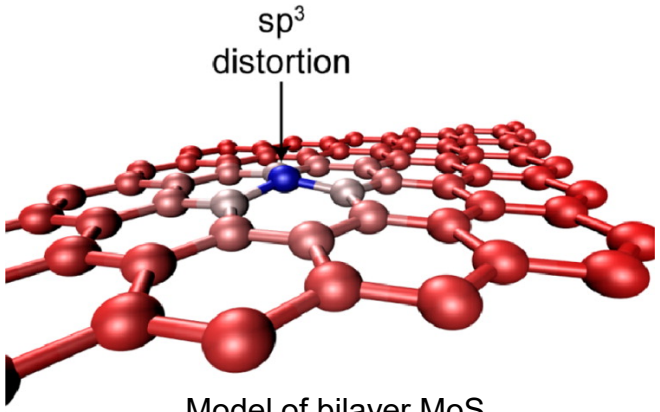


Model of bilayer MoS_2

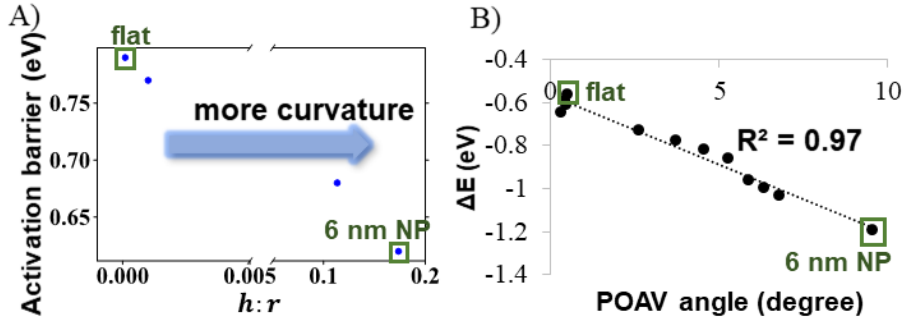
Summary

- Computationally determined that an increase in curvature of graphene leads to a decreased in-plane electron delocalization, lowering the activation barrier for functionalization with 4-NBD

- Experimentally show that an increase in the curvature of the graphene lattice, leads to an increase of reactivity of graphene

- Plan to describe the adsorption of water and oxygen on MoS_2 and their effect on the tribological properties.

- Plan to describe the effects of layer thickness, metal substrate, and strain on the adsorption of water and oxygen on MoS_2



Postulate that new science may be pushed forward by investigating changes in the reactivity of 2D-materials as a function of precise out-of-plane distortion of the basal plane

Acknowledgements

Research Team	Collaborators	Funding
TAMU Dr. James D. Batteas (Advisor) Dr. Sarbajit Banerjee (Committee Member) Dr. Perla Balbuena (Committee Member) Dr. Daniel Tabor (Committee Member) Dr. Cody Chalker (UC Davis) Dr. Meagan Elinski (Hope College) Dr. Zhoutong Liu (Frontage Laboratories) Batteas Group: Maelani Negrito, Fanglue Wu, Nate Hawthorne, Xinyuan Chen, Noah Sheehan, Mckenzie Pedley	**Sandia National Labs** Dr. Mike Chandross Dr. Nicolas Argibay Dr. John F. Curry Dr. Michael Wolfe Dr. Scott Bobbitt **UPenn** Dr. Andrew Rappe Dr. Sayan Banerjee	DOE CSGF Sandia National Laboratories CMCC

Thank you for your time! Any questions?