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

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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$_2$O)
- Summary and Acknowledgements
Two-Dimensional (2D) Materials

- NASA Dry Lubricant Smooths the Way for Space Travel, Industry

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

- Solid dry lubricant
- Anti-wear performance

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

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

Graphene: planar six membered sp² carbon ring highlighted in red
Molybdenum disulfide (MoS₂)

- 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


Challenges of 2D Material Chemistry

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

Tunable electronic and optical properties

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


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: - $1 \times 10^7$ bar* Å$^3$ to $1 \times 10^7$ bar* Å$^3$).

The chemical reactivity of the basal plane of 2D materials can be modulated by electronic and geometric effects through directed forces.
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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Q1: How does varying mechanical strain of the graphene lattice affect the reactivity of graphene?

- **Tensile Strain**
  - Formation energy decreases as strain increases

- **Compressive Strain**
  - Compressive strains result in enhanced reactivity

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**Modulating Reactivity of Graphene by Application of Strain**

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Bissett, M.; et al. Enhanced Chemical Reactivity of Graphene Induced by Mechanical Strain. ACS Nano. 2013, 7, 10335-10343

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**
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- **Compressive Strain**
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- Lack of systematic control of strain
- Difficulty determining “real” strain
- Decouple substrate effects from strain/reactivity experiments

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

Radical reaction of 4-nitro-benzenediazonium tetrafluoroborate (4-NBD) with graphene
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 $\pi$-orbital axis vector (POAV) angle with the reaction energy ($\Delta E$).
Key Findings

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

Summary of Results

Fig. Z. A) Schematic diagram showing the relative orientation of graphene frontier orbitals. B) Correlation of the POAV angle with the reaction energy ($\Delta E$).
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We see the formation of coherent single-layer 1H-1T MoS$_2$ heterostructures by mechanical exfoliation on Au(111).

Large-scale STM image ($V_{\text{bias}} = +500$ mV, $I_t = 0.5$ nA) of single-layer MoS$_2$ with two different moiré patterns.
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.

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$_2$O, etc.)

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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

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Thank you for your time! Any questions?