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RPPR Final Report
as of 14-Feb-2022

Agency Code: 21XD

Proposal Number: 71816MS **Agreement Number: W911NF-18-1-0367**
INVESTIGATOR(S):

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Organization: **Yale University**
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DUNS Number: 043207562 EIN: 060646973
Report Date: 28-Feb-2022 Date Received: 14-Feb-2022
Final Report for Period Beginning 01-Sep-2018 and Ending 30-Nov-2021
Title: Intercalation in 2D nanomaterials for heterostructures with tunable materials properties
Begin Performance Period: 01-Sep-2018 **End Performance Period:** 30-Nov-2021
Report Term: 0-Other
Submitted By: Jeeyoung Cha Email: judy.cha@yale.edu
Phone: (203) 737-7293
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1 **STEM Participants:** 5

Major Goals: The major goal of the project was to use electrochemical intercalation of alkali metals to modulate and control the electronic properties of two-dimensional (2D) materials and their heterostructures and to induce phase transitions in 2D materials. For this, we built electrochemical cells that combine field effect transistors and electrochemical intercalation for in situ characterization during lithium intercalation. Technologically, the 2D materials that were intercalated with lithium at controlled concentrations could be used for various device applications, including lithium ion battery, memory, and novel superconductor.

Accomplishments: We developed an electrochemical cell that combines field effect transistors with electrochemical intercalation, which allows us to perform various material characterization in situ, as a function of controlled lithium intercalation.

With the electrochemical cell development, we have made several scientific observations.
1. Lithium intercalation can occur through the basal planes of 2D materials, including the wide bandgap semiconductor, hBN (hexagonal boron nitride).

2. Intercalation-induced phase transition in 2D materials can be changed significantly by controlling the heterointerface of 2D materials. We examined the intercalation-induced phase transition of MoS_2 when MoS_2 is interfaced with graphene, hBN, and various substrates. We found that the nucleation barrier is controlled by the interface because the nucleation is a heterogeneous nucleation that starts at the outermost MoS_2 layer.

3. Phase transition kinetics in 2D materials can be controlled by the heterointerface. 2D materials anchored on SiO_2 has the slowest kinetics for the intercalation-induced phase transitions while 2D materials supported on another 2D material has a faster kinetics for phase transition.

4. Lithium intercalation achieves a very high electron doping in 2D materials, much more than ionic liquid gating because lithium ions get inserted in every van der Waals gap of 2D materials in intercalation.

5. Organic electron donors that functionalize the surface of semiconducting 2D materials effectively dopes the 2D materials. We experimentally measured doping powers of several organic electron donors and achieved a record doping level in monolayer MoS_2.

Training Opportunities: All graduate students gave presentations on their research annually at the Materials Research Society (MRS) Fall meetings.

Postdoc Mengjing Wang gave a talk on her research at the 2021 MRS fall meeting and an invited talk at the 2022 TMS meeting.

Undergraduate student Maria gave a research presentation on her research at Yale. Based on her research experience in my group, she wants to pursue research in materials science and applied for the NSF REU program for the summer of 2022.

Graduate student Joshua Pondick successfully defended his PhD in the fall of 2021, and is working as a staff scientist at a battery startup company in Boston, Ambri.

Postdocs Dr. Sajad Yazdani and Dr. Milad Yarali interviewed and started their engineer positions at ASML and Samsung, respectively, in 2020.

Results Dissemination: During the period of funding (September 1, 2018 - November 30, 2021), PI Cha gave 16 departmental seminars and 19 invited talks at workshops and conferences on the ARO-funded research.

Graduate students and postdocs gave research presentations (either poster presentations or talks) at least once a year at MRS or APS meetings.

8 peer-reviewed papers were published, which acknowledge the support of the ARO funds. We anticipate 3 more papers to be published in 2022.

Honors and Awards: PI Judy Cha received the Young Innovator Award in Nano Energy by Nano Research in 2019, the EPiQS (Emergent Phenomena in Quantum Systems) Materials Synthesis Investigator Award by Gordon and Betty Moore Foundation in 2019, and the Young Faculty Award by Semiconductor Research Corporation in 2021.

Graduate student Josh Pondick received the National Defense Science and Engineering Graduate Fellowships (NDSEG) in 2018. Graduate student Serrae Reed received an honorable mention in 2020 for her National Science Foundation Graduate Student Fellowship application.

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Jeeyoung (Judy) Cha
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Sajad Yazdani
Person Months Worked: 10.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Milad Yarali
Person Months Worked: 11.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Serrae Reed
Person Months Worked: 5.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
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Person Months Worked: 5.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Shiyu Xu
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
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Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Maria Bambrick-Santoyo
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Joshua Pondick
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

ARTICLES:

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Volume: 7 Issue: 3 First Page #: 030902
Date Submitted: 5/10/19 12:00AM Date Published: 3/1/19 5:00AM
Publication Location:
Article Title: The development of 2D materials for electrochemical energy applications: A mechanistic approach
Authors: David J. Hynek, Joshua V. Pondick, Judy J. Cha
Keywords: intercalation, 2D materials
Abstract: Energy production and storage is one of the foremost challenges of the 21st century. Rising energy demands coupled with increasing materials scarcity have motivated the search for new materials for energy technology development. Nanomaterials are an excellent class of materials to drive this innovation due to their emergent properties at the nanoscale. In recent years, two dimensional (2D) layered materials have shown promise in a variety of energy related applications due to van der Waals interlayer bonding, large surface area, and the ability to engineer material properties through heterostructure formation. Despite notable results, their development has largely followed a guess and check approach. To realize the full potential of 2D materials, more efforts must be made towards achieving a mechanistic understanding of the processes that make these 2D systems promising. In this perspective, we bring attention to a series of techniques used to probe fundamental energy related processes
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
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Volume: Issue: First Page #:
Date Submitted: 5/10/19 12:00AM Date Published: 4/1/19 12:00AM
Publication Location:
Article Title: Recent progress on in situ characterizations of electrochemically intercalated transition metal dichalcogenides
Authors: Sajad Yazdani, Milad Yarali, Judy J. Cha
Keywords: transition metal dichalcogenides, electrochemical intercalation, in situ characterizations, transmission electron microscopy (TEM), magnetotransport measurements
Abstract: Layered transition metal dichalcogenides (TMDCs) have been extensively studied owing to their unique physical and chemical properties. Weak van der Waals (vdW) interactions between the stacking layers of TMDCs allow intercalation of various species including monovalent alkali, divalent alkaline earth and multivalent metal ions, zero-valent transition metals, as well as organic molecules, all of which can drastically alter fundamental properties of the TMDCs. The urge to understand the phenomena and the desire to exploit them for applications have inspired a great deal of investigations. A large portion of the mystery has been unveiled over the past decade of intense research; however, many questions remain open and require further explorations. This review is concerned with investigations on structural and electronic evolution of TMDCs driven by electrochemically controlled intercalations. Herein, we aim to survey the recent advances and experimental platforms for monitoring the interc
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Acknowledged Federal Support: **Y**

Partners

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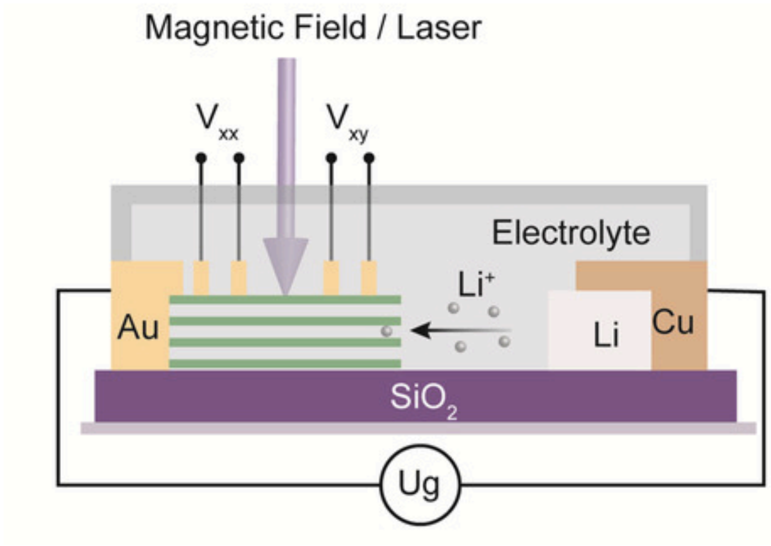
I certify that the information in the report is complete and accurate:
Signature: Jeeyoung Cha
Signature Date: 2/14/22 3:09PM

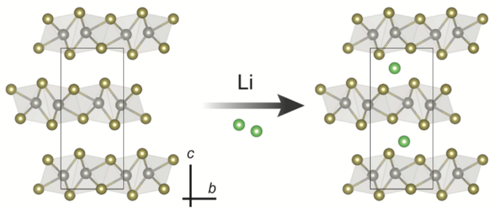
Intercalation in 2D nanomaterials for heterostructures with tunable materials properties

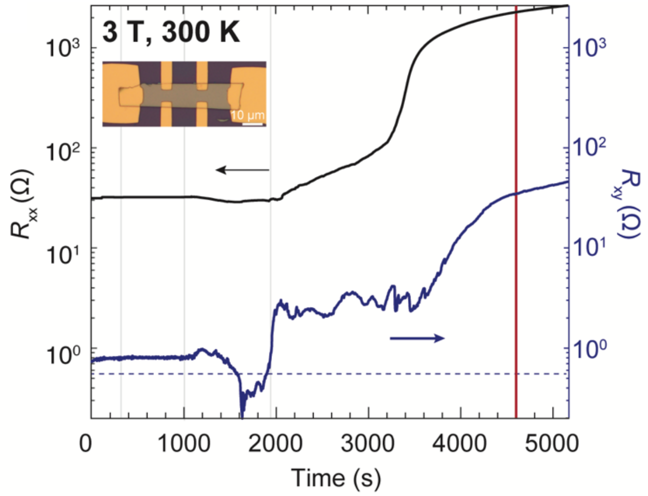


W911NF-18-1-0367

Judy (Jeeyoung) Cha

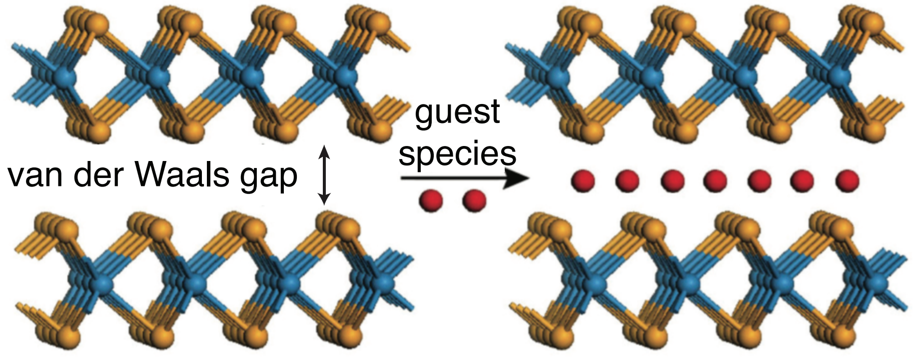
Yale University

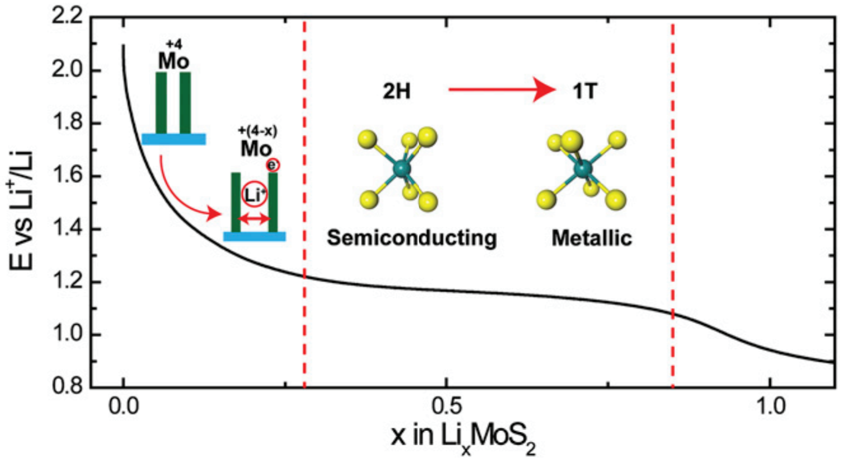




Background

Layered TMDs can host intercalants in vdW gaps for property tuning and emergent electronic phases.





PNAS **2013**, 110, p.19701-19706.

Program Goals

Use intercalation to 1. control structure and properties of 2D TMDs,
2. understand vdW forces and stresses in 2D materials.

Aim 1: Understand intercalation induced phase transition in 2D TMDs.

Aim 2: Use intercalation to construct a stack of monolayer TMDs with desirable properties and encapsulation.

Aim 3: Use intercalation to probe vdW forces and stresses on materials properties via *in situ* TEM.

Progress on Program Goals

Use intercalation to 1. control structure and properties of 2D TMDs,
2. understand vdW forces and stresses in 2D materials.

✓ **Aim 1**: Understand intercalation induced phase transition in 2D TMDs.

- Interfacial and confinement effects on the 2H-1T' phase transition of MoS_2
  → The phase transition proceeds via heterogeneous nucleation of 1T' phase.
- Intercalation induced phase transition in Td-WTe_2 and 1T'-$MoTe_2$
  → Unexpected gapped, semiconducting phase by lithium intercalation.

✓ **Aim 2**: Use intercalation to construct a stack of monolayer TMDs with desirable properties and encapsulation.

- Molecular doping to control carrier density of monolayer MoS_2 and to provide encapsulation
  → Record high carrier densities (1×10^{14} cm^{-2} in MoS_2).

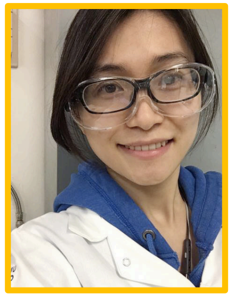
✓ **Aim 3**: Use intercalation to probe vdW forces and stresses on materials properties via *in situ* TEM

- Effects of strain on intercalation kinetics in graphene

Scientific and Technological Transitions

Aims 1 & 3


Dr. Yazdani


Dr. Wang


J. Pondick


S. Xu

Aim 2


Dr. Yarali


S. Reed


N. Williams

Collaborators

Diana Qiu (Yale MEMS)
Dr. Aakash Kumar

Nilay Hazari (Yale Chemistry)
Dr. David J. Charboneau
Julia B. Curley

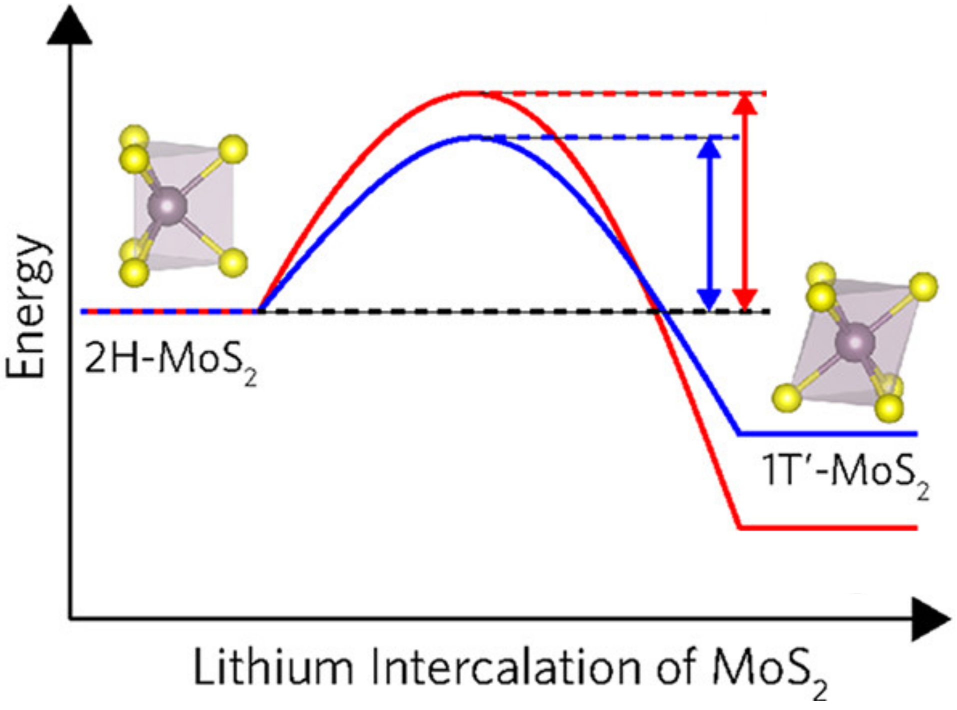
Hailiang Wang (Yale Chemistry)
Dr. Yiren Zhong

Su-Ying Quek (National U of Singapore)
Dr. Yifeng Chen

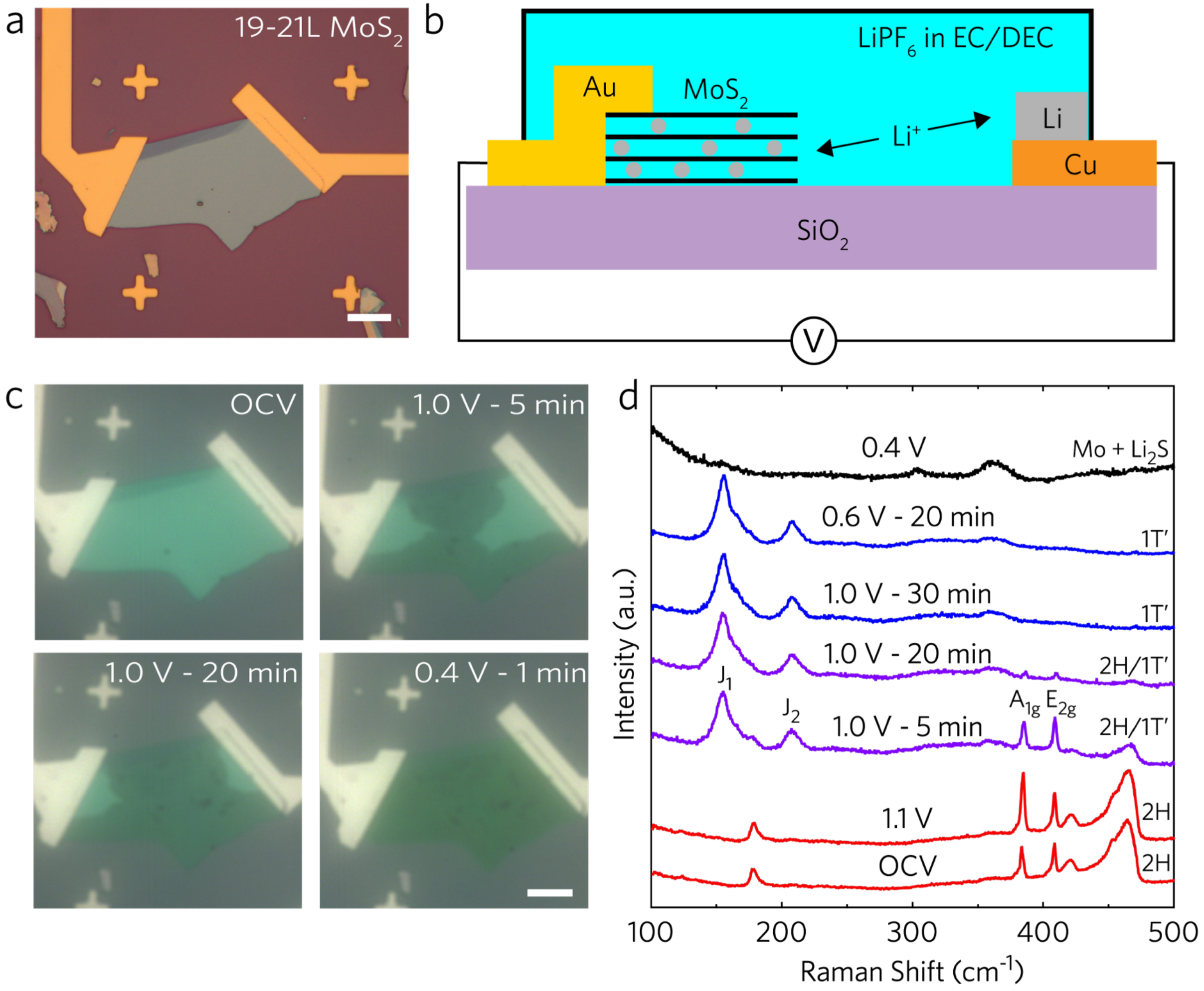
Peijun Guo (Yale CHEM)
Dr. Hao Dong

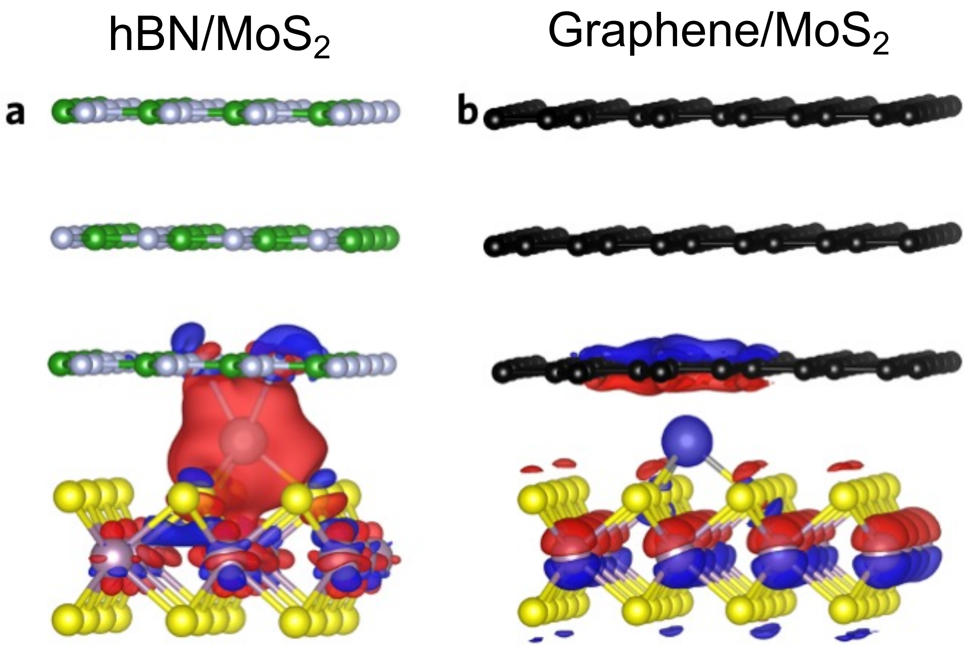
Aim 1. Heterogeneous Nucleation of 1T’ Phase in MoS_2

What is the nucleation pathway?



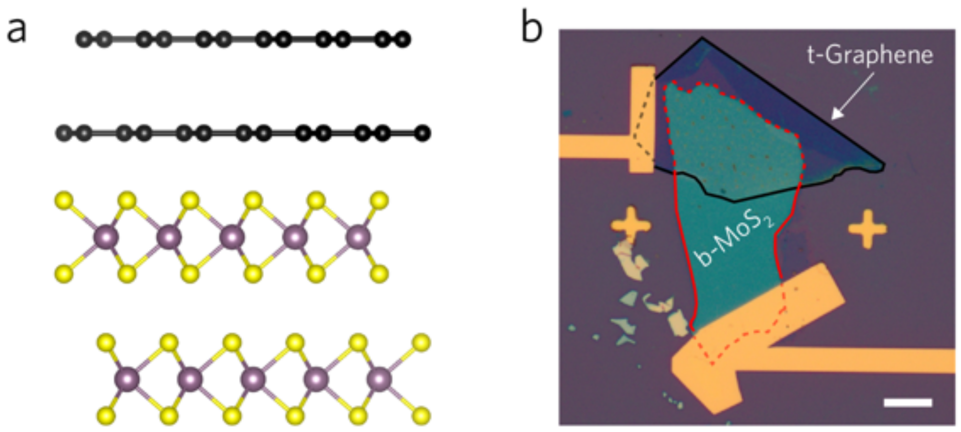
2H-1T’ at 1.0 – 1.1 V vs. Li/Li⁺.



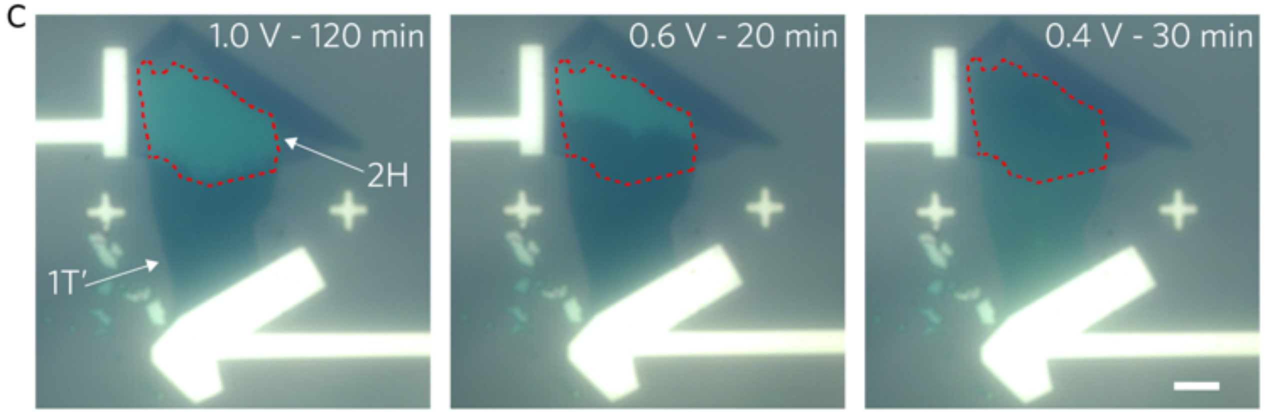


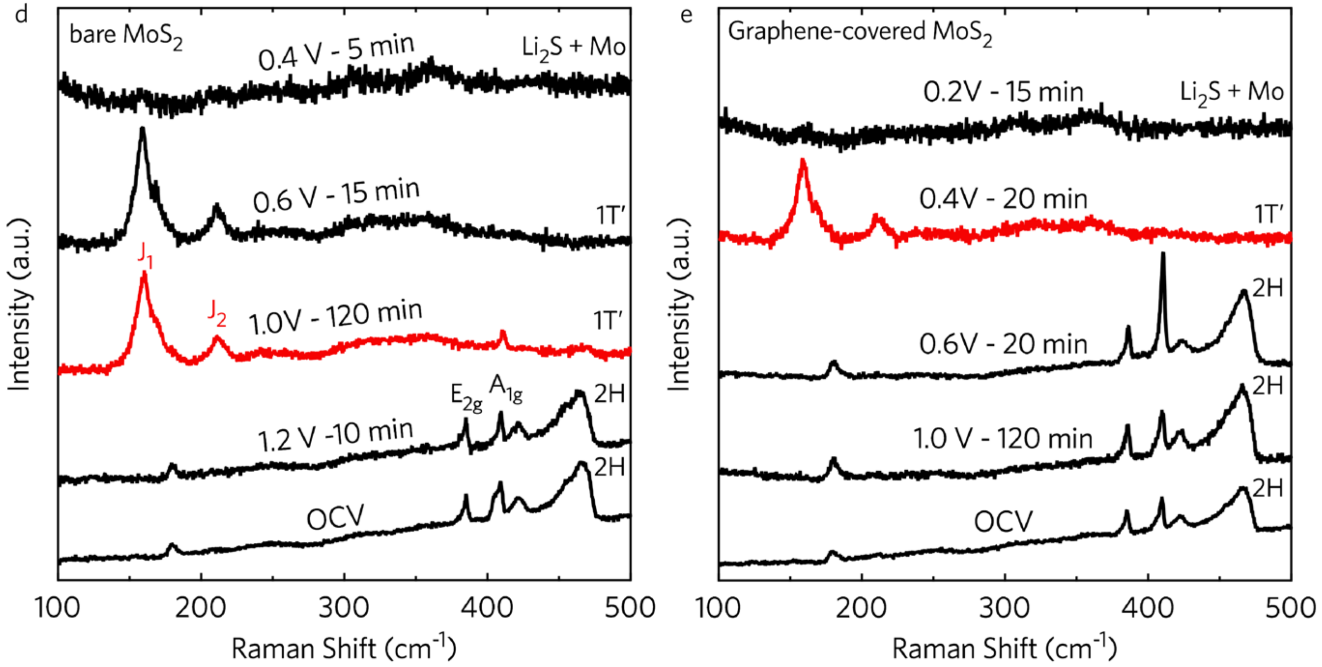
e^- transfer from Li to MoS_2 and graphene at interface.

→ Higher [Li^+] for phase change in graphene/MoS_2.



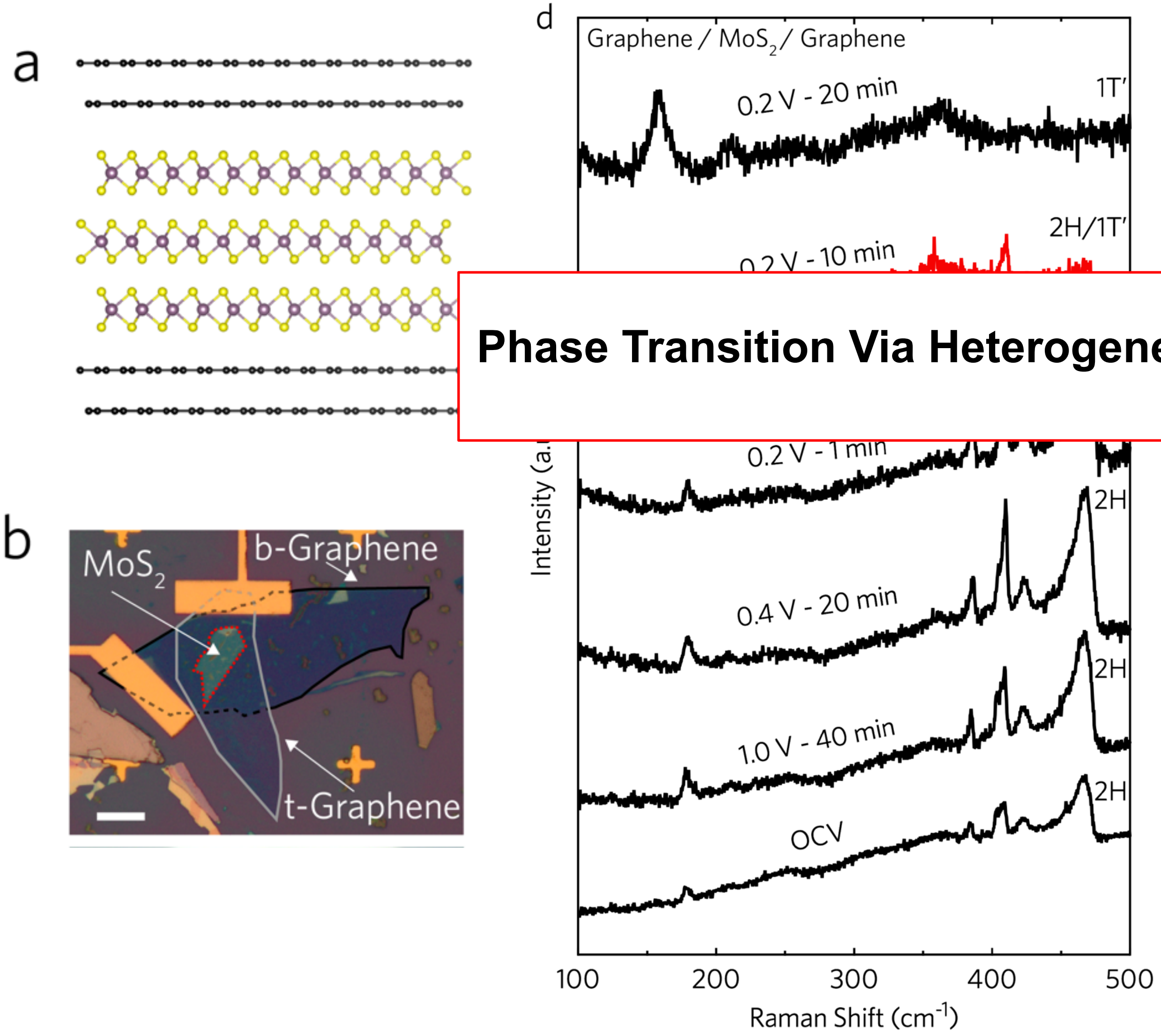
- **Bare MoS_2: 1.0 V**
- **Graphene / MoS_2 : 0.4 V**



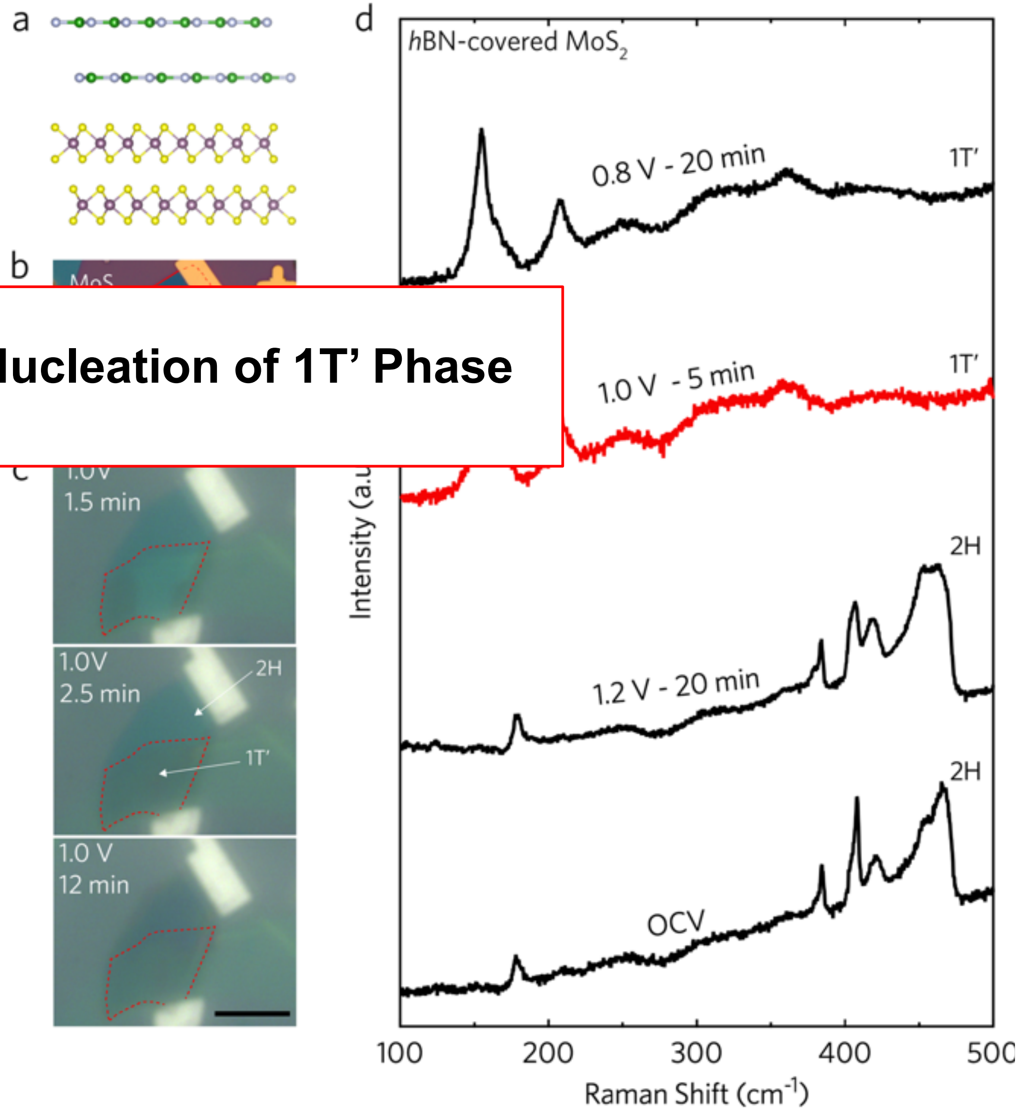


Heterogeneous Nucleation of 1T' Phase in MoS_2 (Aim 1)

G / MoS_2 / G

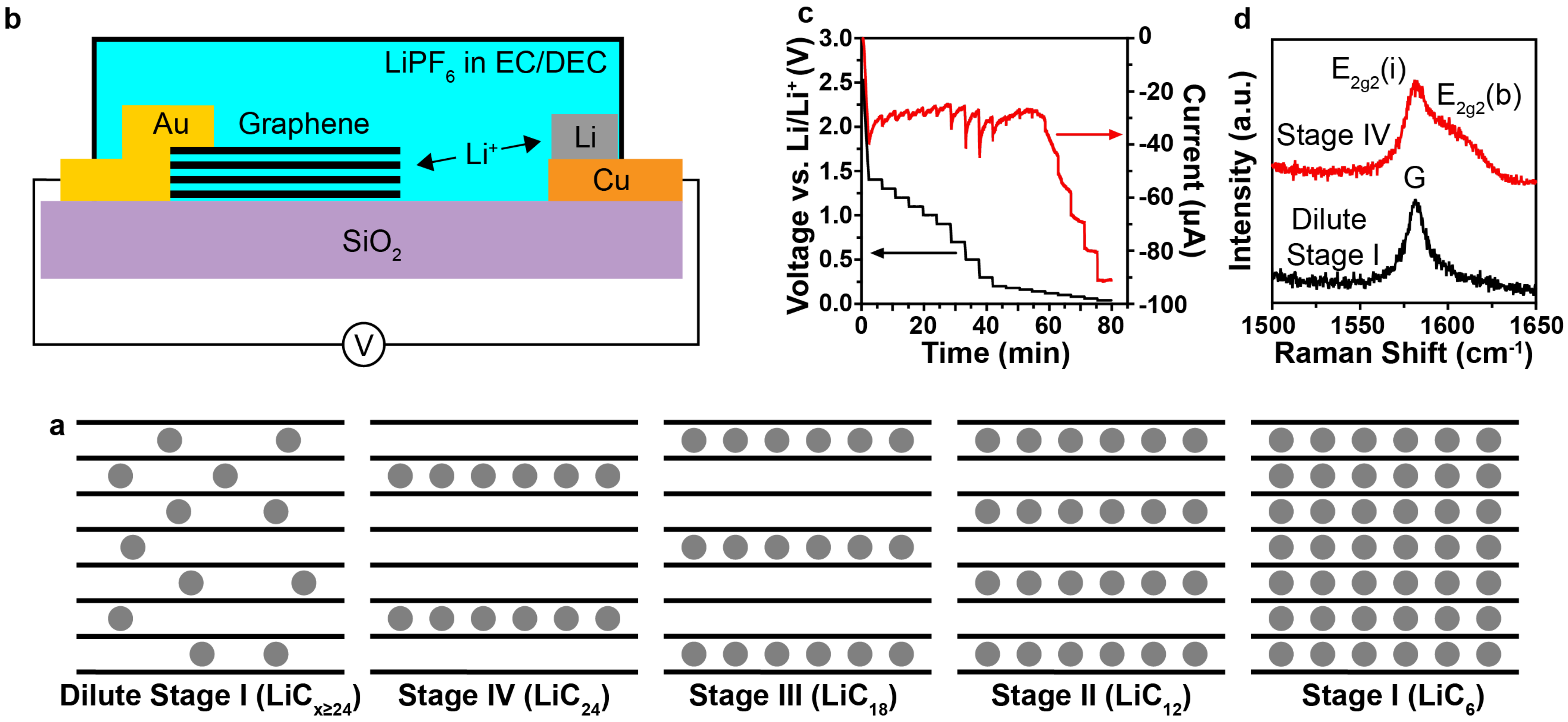


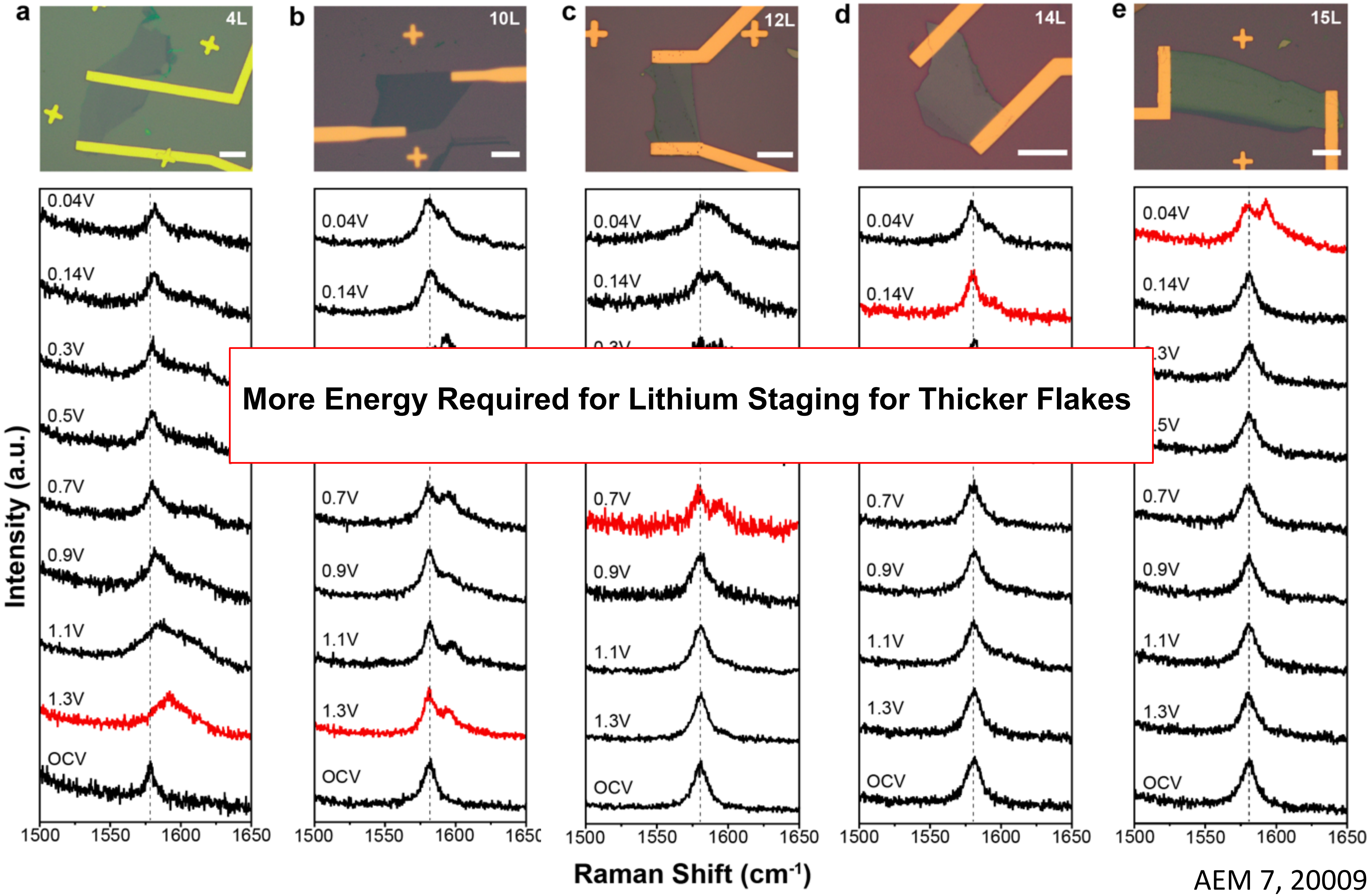
hBN / MoS_2 / hBN



Phase Transition Via Heterogeneous Nucleation of 1T' Phase

Aim 3. Strain Effects on Lithium Staging in Graphene

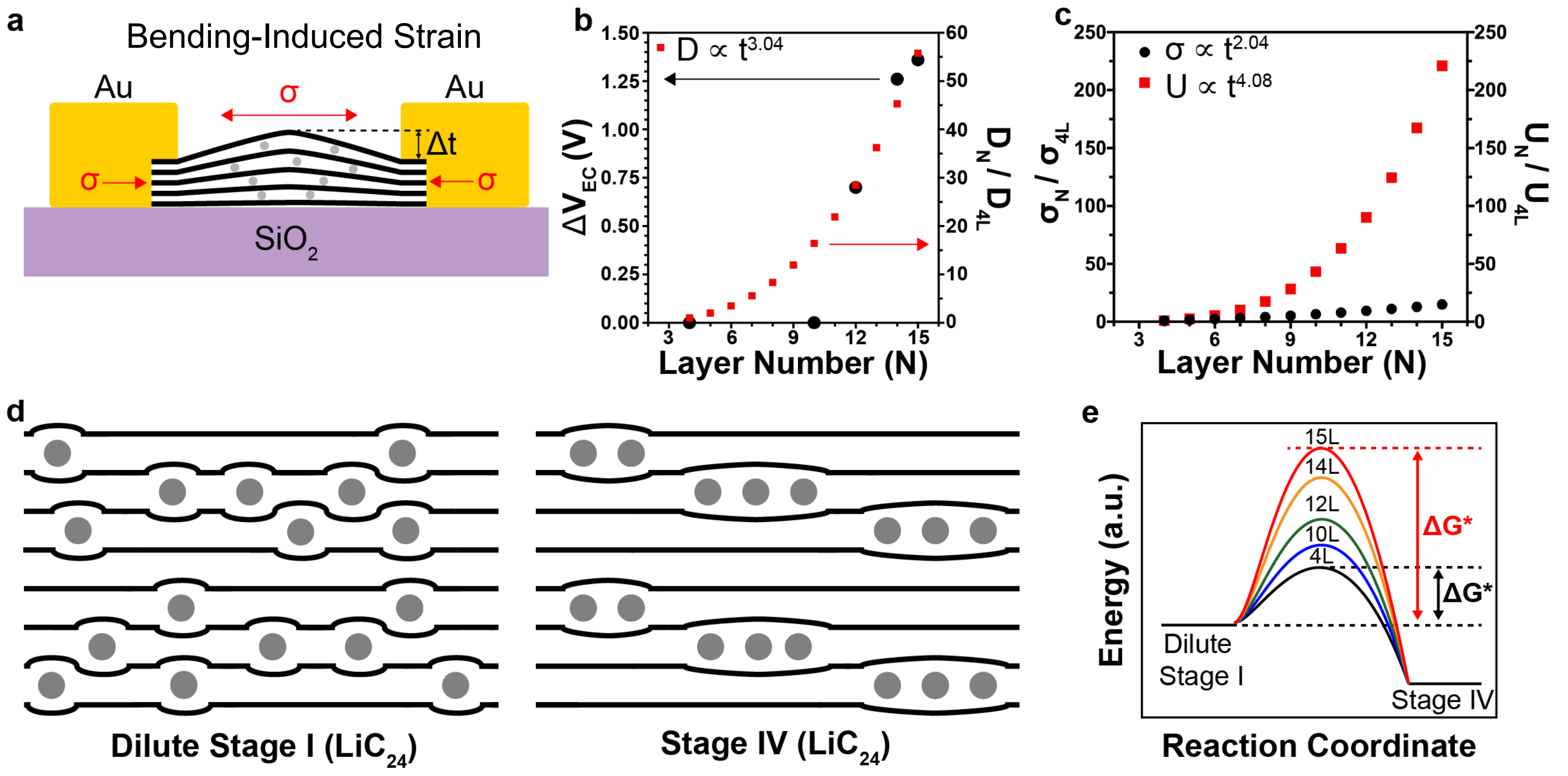




More Energy Required for Lithium Staging for Thicker Flakes

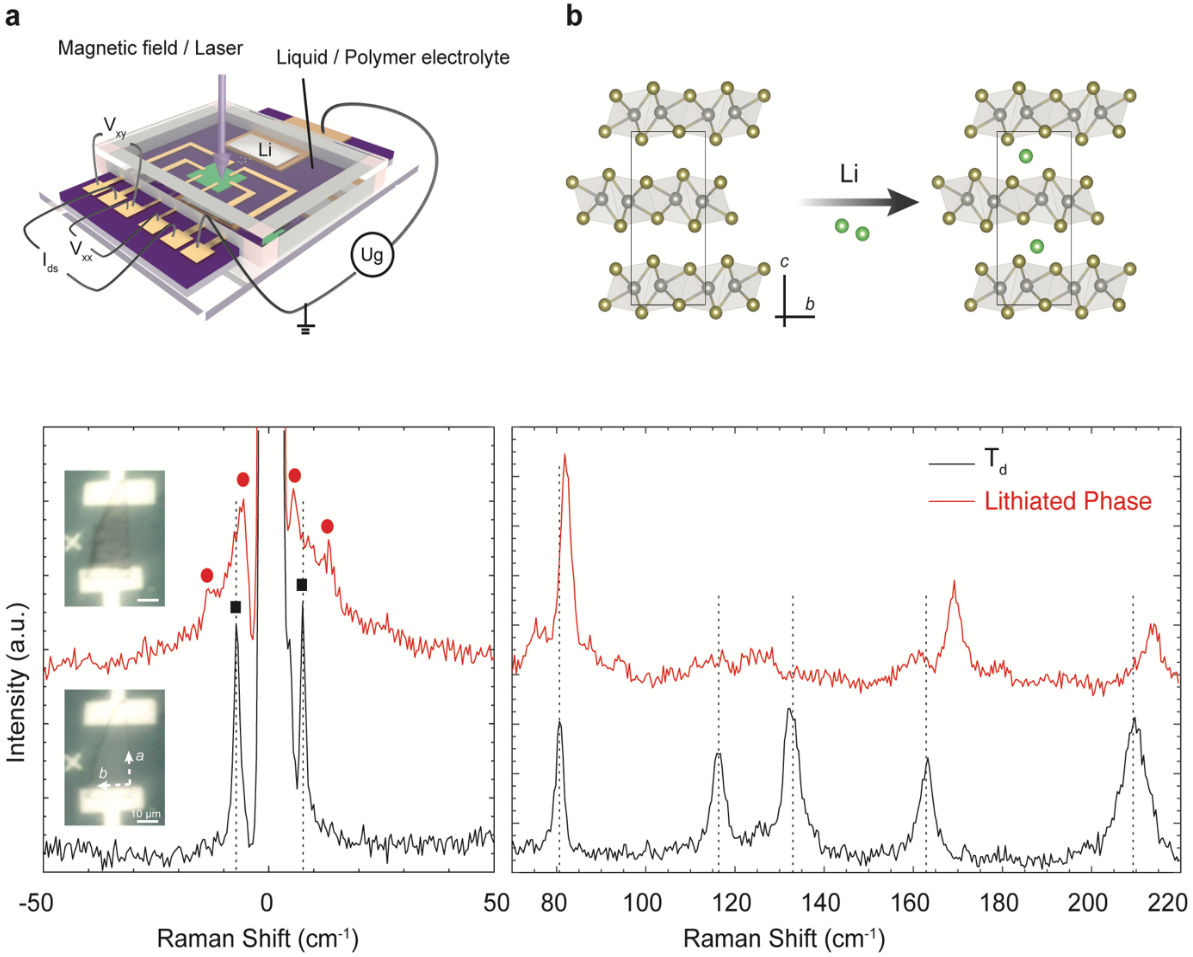
AEM 7, 2000981 (2021)

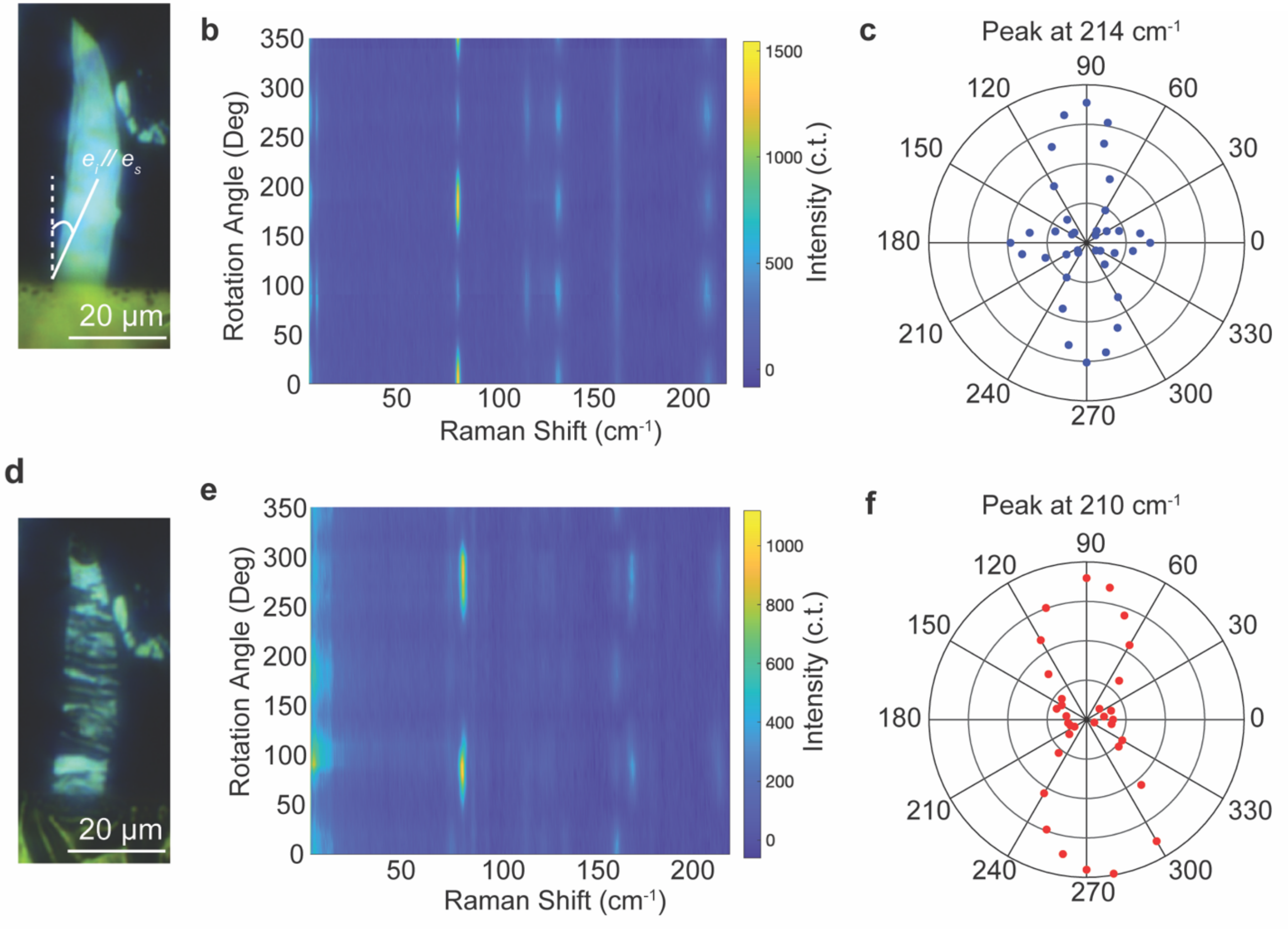
Induced Strain Increases Nucleation Barrier (Aim 3)



AEM 7, 2000981 (2021)

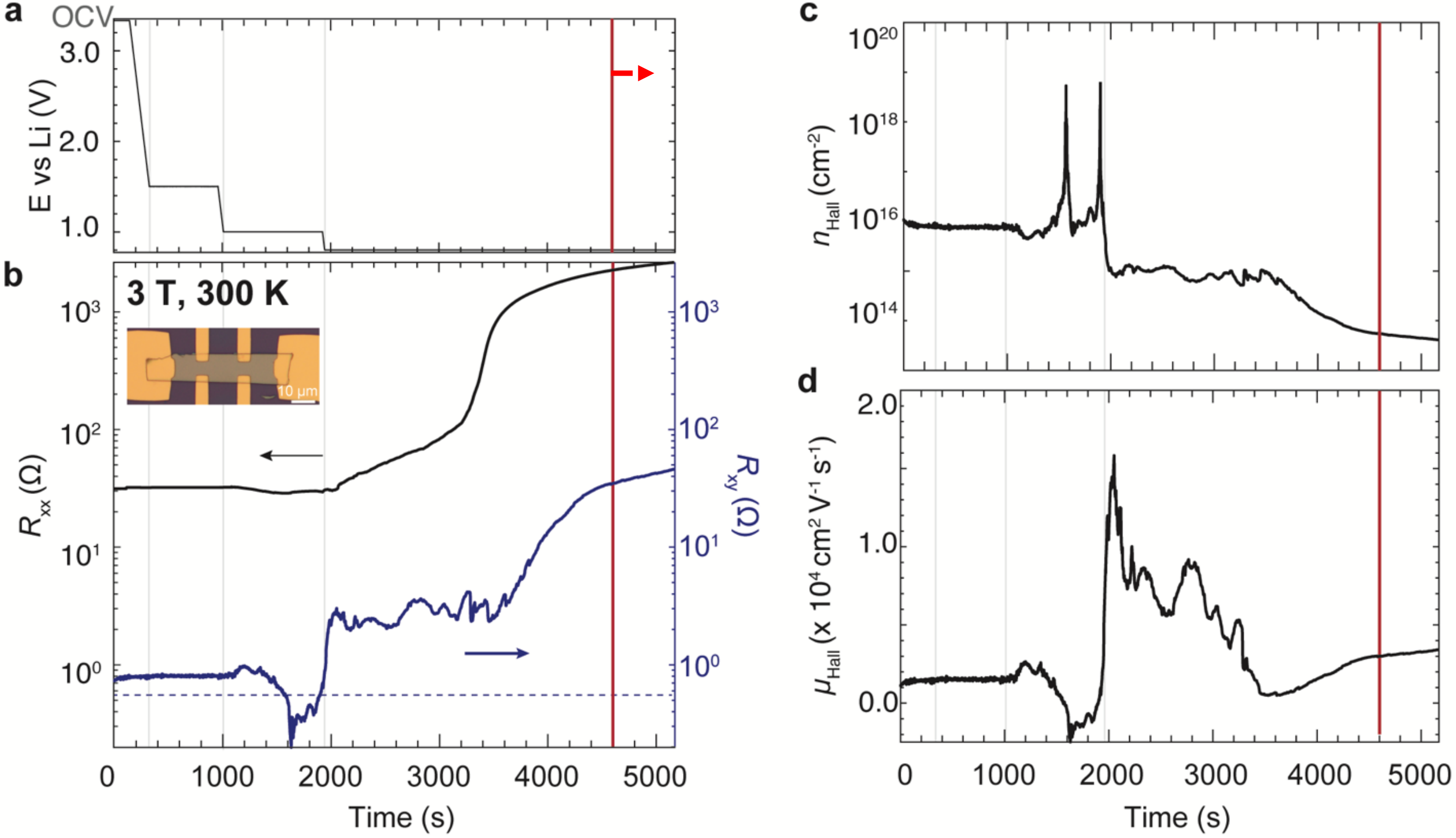
Intercalation Induced Novel Phase in WTe_2 (Aim 1)



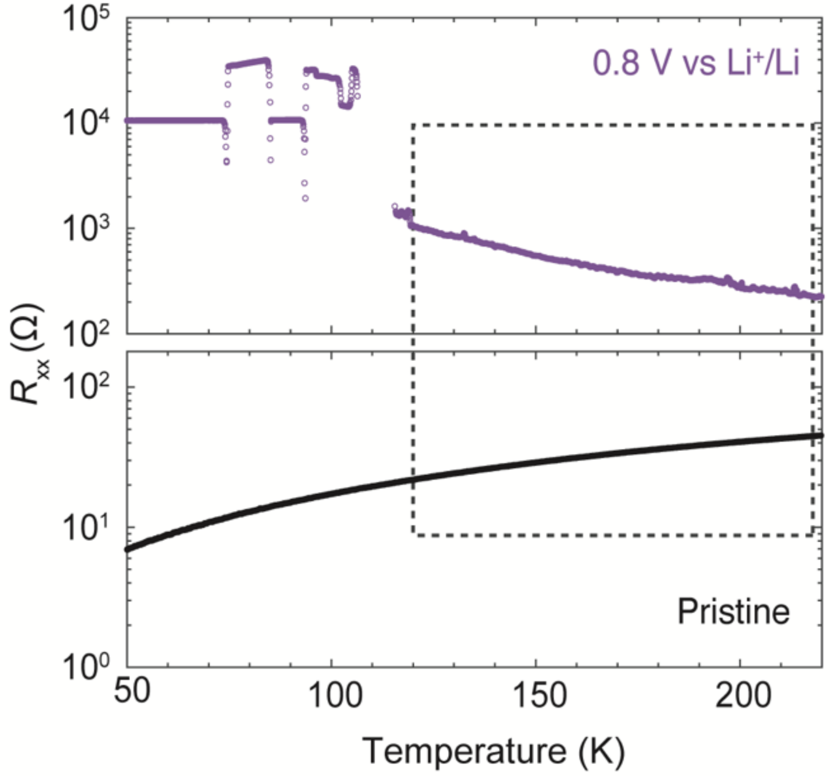


Lindenberg et. al., *Adv. Mater*. **2021**, 2101875

Metal – Insulator Phase Transition in WTe_2



New phase



ARO-Funded Publications (09/2018-present)

Published or under revision

1. **Heterointerface control over lithium-induced phase transitions in MoS_2 heterostructures**
   arXiv:2107.02255 (2021)
2. **Molecular surface functionalization: A pathway for magnetic property tuning of 2D materials**
   Adv. Mater. Inter. **2021**, under revision.
3. **Revisiting intercalation-induced phase transitions in 2D group VI transition metal dichalcogenides**
   Adv. Ener. & Sustain. Res. **2021**, doi:10.1002/aesr.202100027.
4. **The effect of mechanical strain on lithium staging in graphene**
   Adv. Elect. Mater. **2021**, 7, 2000981.
5. **Heterointerface effects on lithium-induced phase transitions in intercalated MoS_2**
   ACS Appl. Mater. Inter. **2021**, 13, p.10603-10611.
6. **Near-unity molecular doping efficiency in monolayer MoS_2**
   Adv. Elect. Mater. **2021**, 7, 2000873.
7. **Recent progress on *in situ* characterizations of electrochemically intercalated transition metal dichalcogenides**
   Nano Res. **2019**, 12, p.2126-2139.
8. **The development of 2D materials for electrochemical energy applications: A mechanistic approach**
   APL Mater. **2019**, 7, 030902.

Submitted or in preparation

9. **Effects of steric factors on molecular doping to MoS_2 (2021)**
10. **Thickness-dependent phase transition kinetics in lithium-intercalated MoS_2 (2021)**
11. **Semimetal to semiconducting phase transition in T_d-WTe_2 by lithium intercalation (2021)**
12. **Lithium intercalation induced phase transition in 1T’-$MoTe_2$ (2021)**

Intercalation in 2D nanomaterials for heterostructures with tunable materials properties

Judy J. Cha, Yale University

ARO Grant #W911NF-18-1-0367

RESEARCH OBJECTIVE and CURRENT STATE-OF-THE-ART

The research objective is to understand the thermodynamics of intercalation induced phase change in 2D materials for optimized and novel property tuning and emergent phases.

Current state-of-the-art approach to understanding intercalation physics and dynamics would be pump-probe measurements during intercalation, *in situ*. Our micro-reactor nanodevice cells enable *in situ* characterization of intercalation dynamics, compatible with pump-probe techniques.

SCIENTIFIC QUESTIONS

Basic science questions we asked in this research were:

1. What are the critical intercalant concentrations that induce phase change in various TMDs?
2. How do properties of TMDs continuously change with the intercalant concentration?
3. What can the intercalant diffusion kinetics tell us about vdW forces and defect-induced stress?

The micro-reactor nanodevice cells allowed us to systematically investigate these scientific questions.

TECHNICAL APPROACH:

- Constructed **micro-reactor nanodevice cells** to investigate intercalation physics and intercalation induced property changes in 2D materials.
- **Remaining tasks to be performed:**
  1. Electrical properties of the intercalation-induced, new phase of $MoTe_2$ need to be measured.
  2. There remains two manuscripts that need to be written.
  3. Adapt the **micro-reactor cells** to be compatible with ***in situ* TEM studies** of intercalation.

RESEARCH ACCOMPLISHMENTS:

- Experimentally observed that in-plane strain decelerates the kinetics of intercalant ordering in graphite.
- Found that intercalation induced phase transition in 2D materials proceeds by heterogeneous nucleation of the new phase. Thus, the nucleation barrier for the intercalation induced phase transition can be tuned by constructing 2D heterostructures.
- Achieved a record high carrier concentration in monolayer MoS_2 with organic dopants, and experimentally measured their doping powers.
- Discovered a new electronic phase by lithium intercalation in WTe_2 and $MoTe_2$.

SCIENTIFIC IMPACT and ARMY/DoD RELEVANCE

The **scientific impact** of the work is in the discovery of unexpected semiconducting phases in semi-metallic 2D tellurides by lithium intercalation and in the finding that the intercalation induced phase transition proceeds via heterogenous nucleation of the new phase at the top or bottom most layer of 2D materials.

The **ARMY/DoD relevance** is that the findings in this work can lead to new electronic devices that utilize intercalation-tuned properties of 2D materials.

INTERACTIONS, COLLABORATIONS, and TRANSITIONS

- The project benefited from having multiple collaborators. They are:
- **Diana Qiu** (Yale) for DFT calculations for intercalation projects,
- **Peijun Guo** (Yale) for optical spectroscopy for intercalation projects,
- **Nilay Hazari** (Yale) for novel organic dopants,
- **Su Ying Quek** (NUS) for DFT calculations for molecular doping of 2D materials,
- **Hailiang Wang** (Yale) for interfacing organic dopants to 2D materials.
- This project did not have collaborations with DoD lab scientists or industry.