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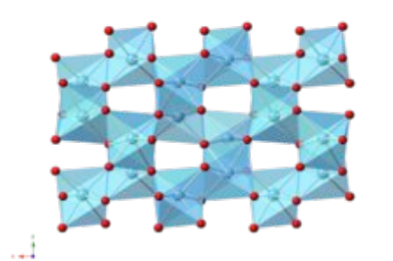
Low-Energy Electron Microscopy (LEEM) Studies of TiO_2(B) Nanosheets Deposited by Langmuir-Blodgett Technique

EFRC CST

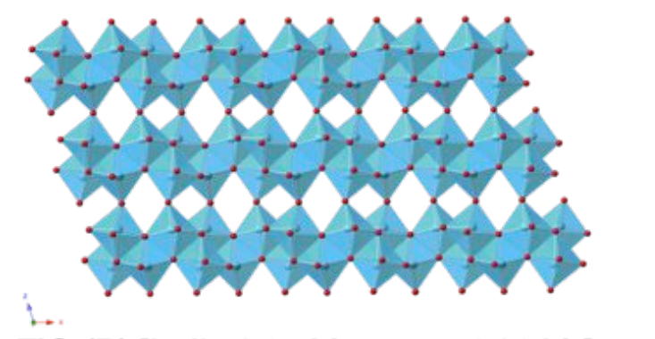
Background

Nanostructured TiO_2 for Electrical Energy Storage

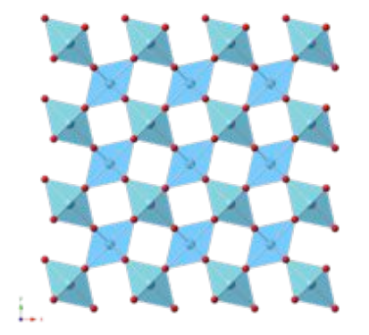
- Nanostructured TiO_2 is a potential replacement for graphite anodes in Li-ion batteries.
  - Higher operating potential for better safety. 1.7 V vs. 0.5 V w.r.t. Li/Li^+
  - Higher capacity at high charge/discharge rates. 420 mAh/g theoretical vs. 350 mAh/g
  - Minimal solid-electrolyte interphase (SEI).
  - Better long-term stability.
- TiO_2(B) polymorph has particular promise due to more open crystal structure.
  - Higher capacity.
  - Faster lithiation kinetics.
  - Potentially faster charge cycles.
  - Strong surface pseudocapacitive behavior – good for hybrid battery/capacitor applications, e.g., supercapacitors.



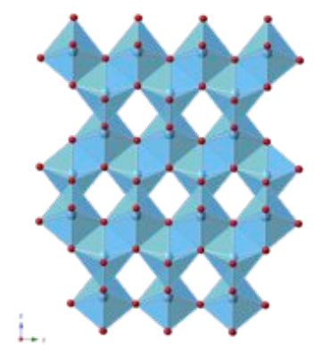
Brookite [bulk=0.1 Li^+, nano=0.5 Li^+]
a = 5.456, b = 9.182, c = 5.143



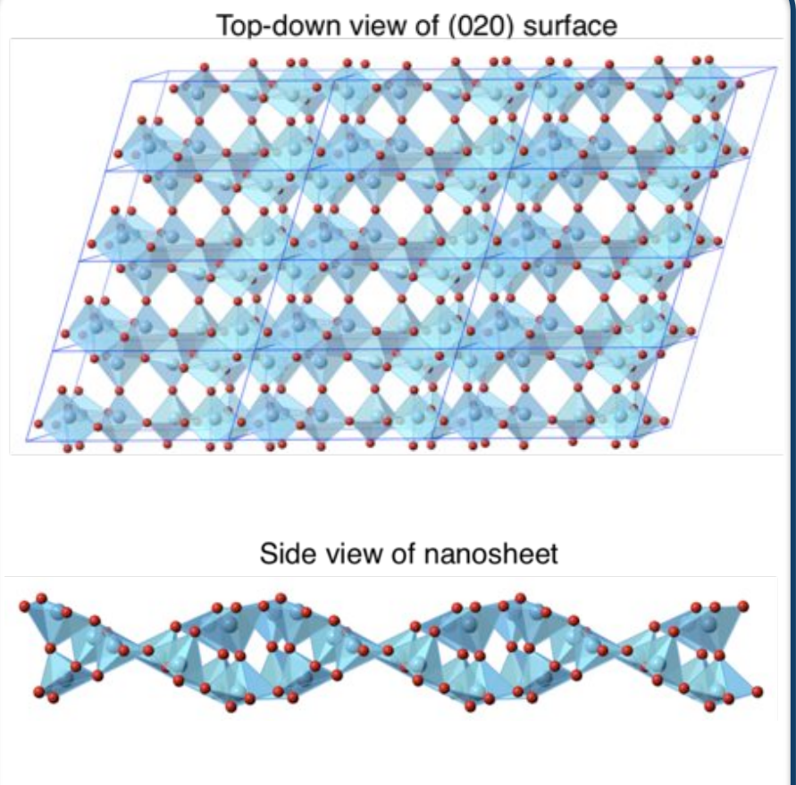
TiO_2(B) [bulk=0.85 Li^+, nano=1.01 Li^+]
a = 12.8, b = 6.52, c = 3.88, b = 107.1



Rutile [bulk=0.1 Li^+, nano=0.75 Li^+]
a = 4.594, c = 2.958

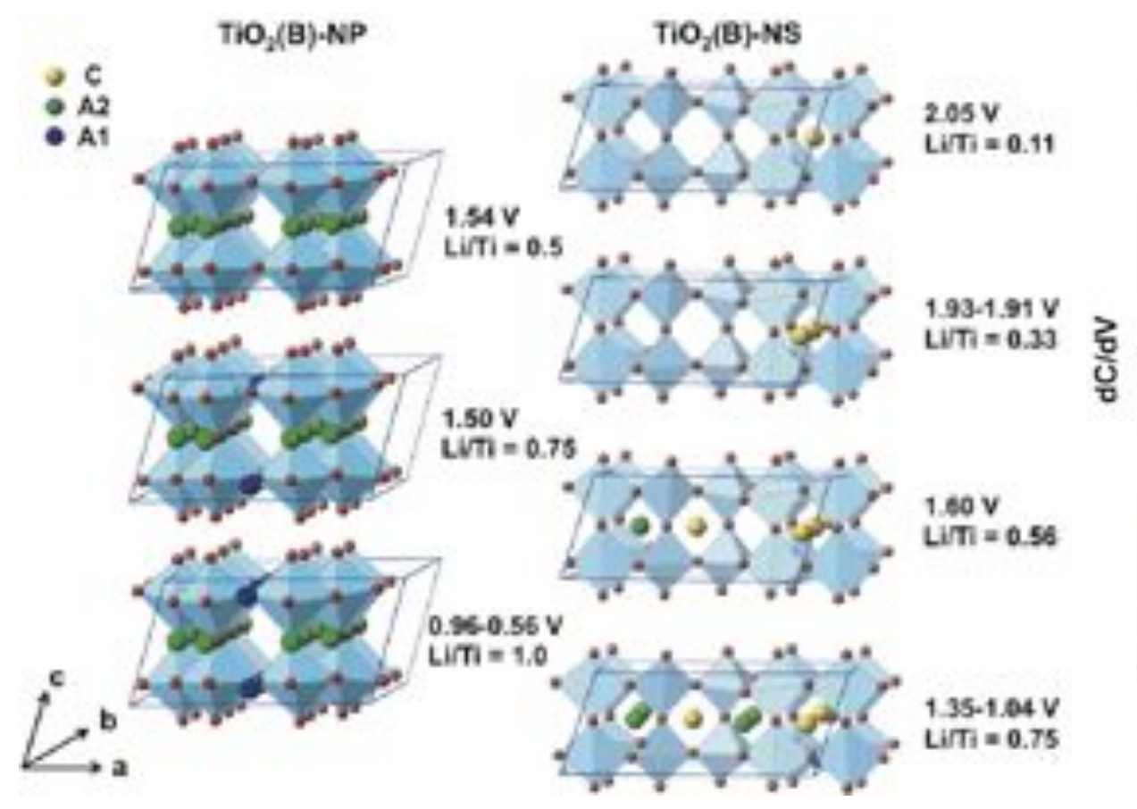


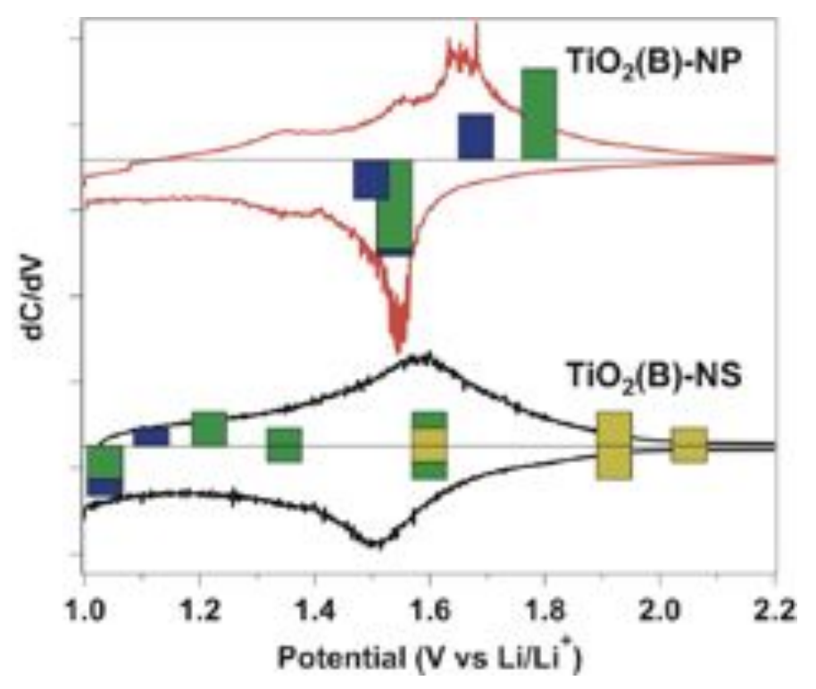
Anatase [bulk=0.5 Li^+, nano=0.85 Li^+]
a = 3.793, c = 9.51



TiO_2(B) [nanosheet = 0.75 Li^+]
a = 13.6, b = 6.28, β = 108.4°

- ***Problem:*** TiO_2 lithiation energetics and kinetics are highly dependent on structure.
  - e.g., Observed in differential capacity plots and DFT+U calculations of TiO_2(B) nanoparticles and TiO_2(B) nanostructures.
- ***Question:*** What are the fundamental microscopic mechanisms and limitations to the lithiation TiO_2 nanostructures?



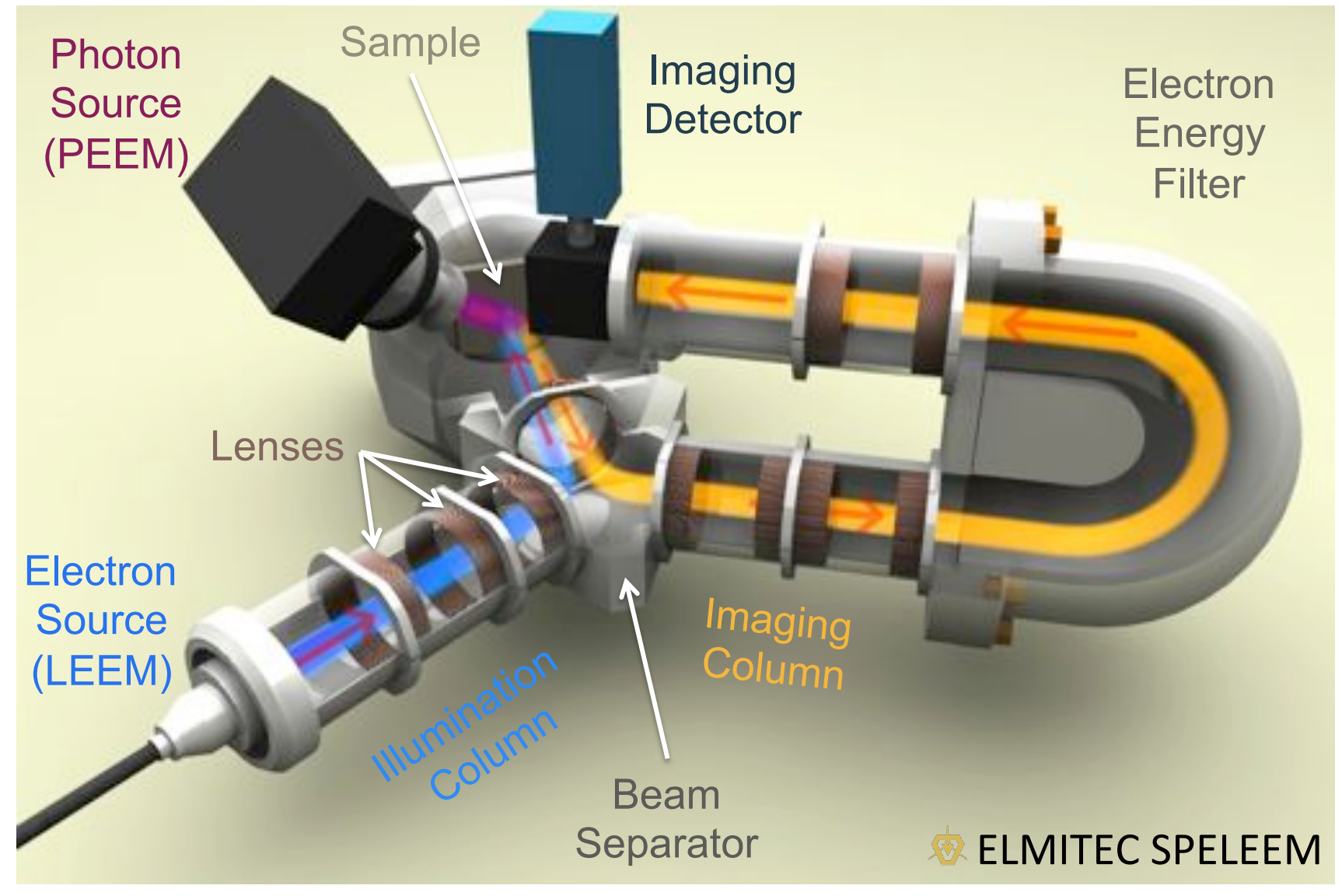


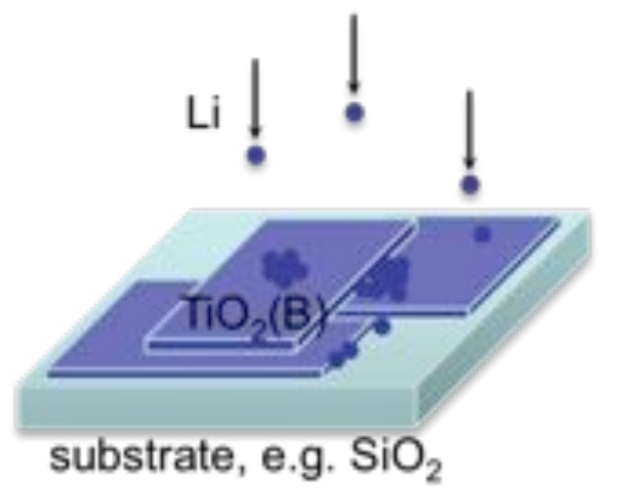
References: Dylla, Xiao, Henkelman, and Stevenson, *J. Phys. Chem. Lett.* 2012, **3**, 2015–2019; Dylla, Lee, and Stevenson, *Langmuir* 2012, **28**, 2897–2903.

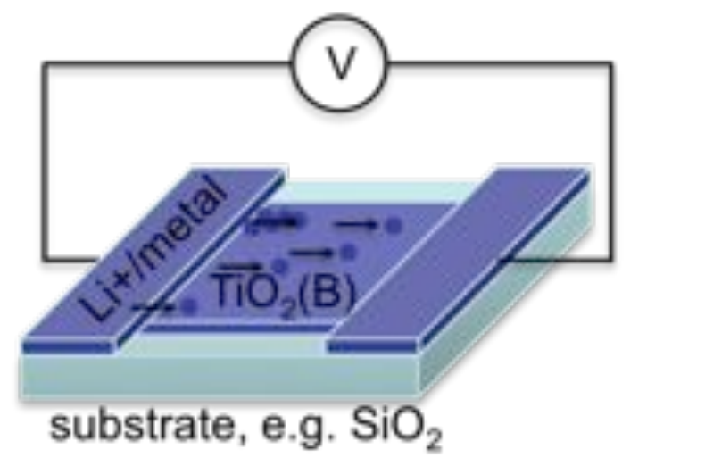
Approach

Low-Energy and Photoemission Electron Microscopy

- LEEM and PEEM image ***real-time dynamic processes at surfaces.***
- Energy filter enables spatially-resolved electron spectroscopy for chemical and electronic structure characterization.
- Real-time study of lithiation and delithiation processes on/in TiO_2.
  - Prepare high-quality TiO_2 films and surfaces.
  - LEEM/PEEM contrast obtained from work function, Ti 3p core level, crystal structure.
  - Observe lithium nucleation and transport.
  - Quantify kinetics and energetics via time and temperature studies.
  - Characterize spatial changes in chemistry, electronic structure, and crystallography.







LEEM/PEEM Capabilities	**Measures**
5-10 nm spatial resolution	Topoolgy
50-100 meV spectral resolution	Chemistry & Electronic Structure
0.5-5 nm depth/surface sensitivity	Surface Crystallography
Electron/Photon/Thermal excitation	Phonons/Plasmons
Real-time imaging, in-situ growth	Carrier/Field Distributions

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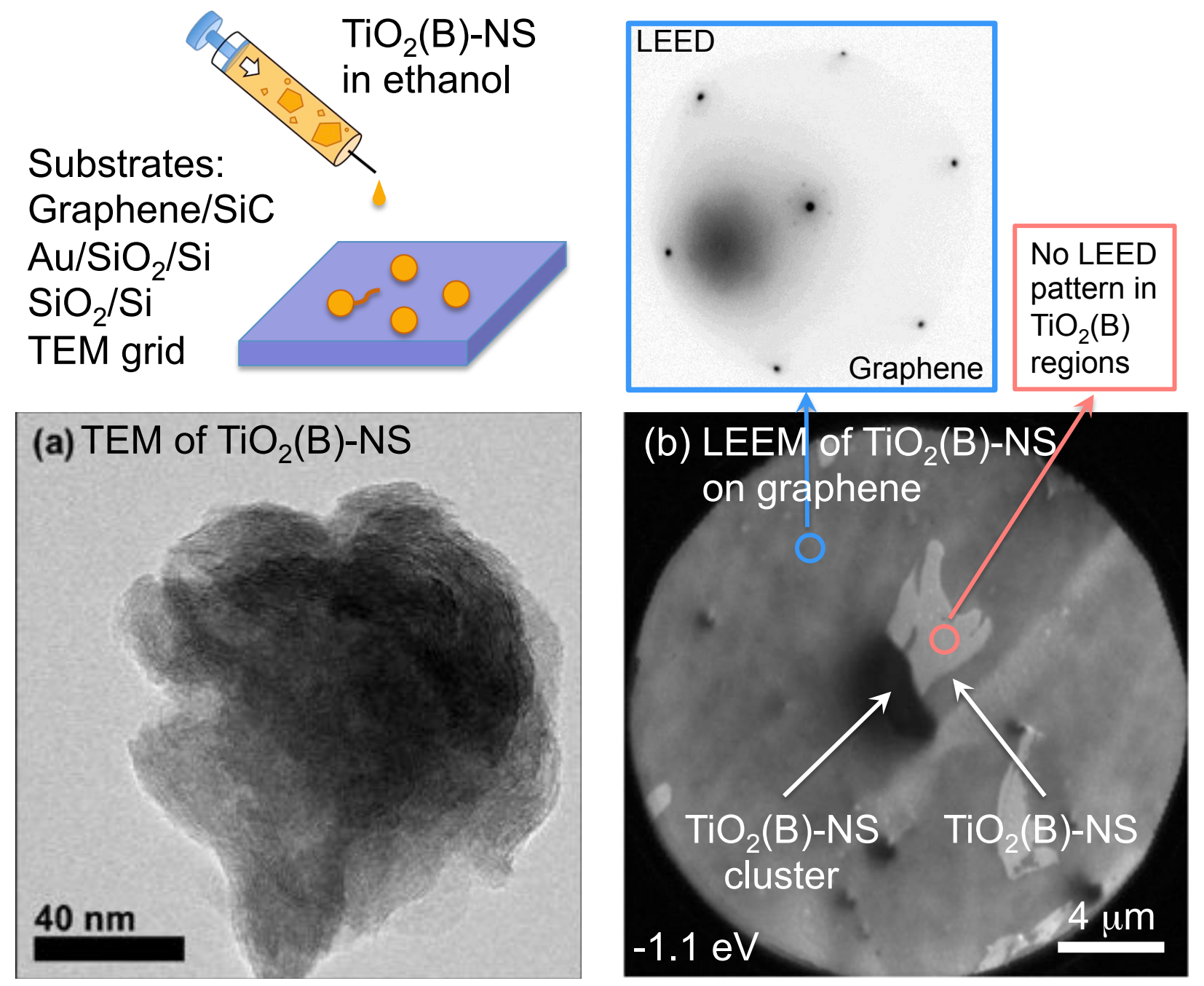
TiO_2(B) Nanosheet Films

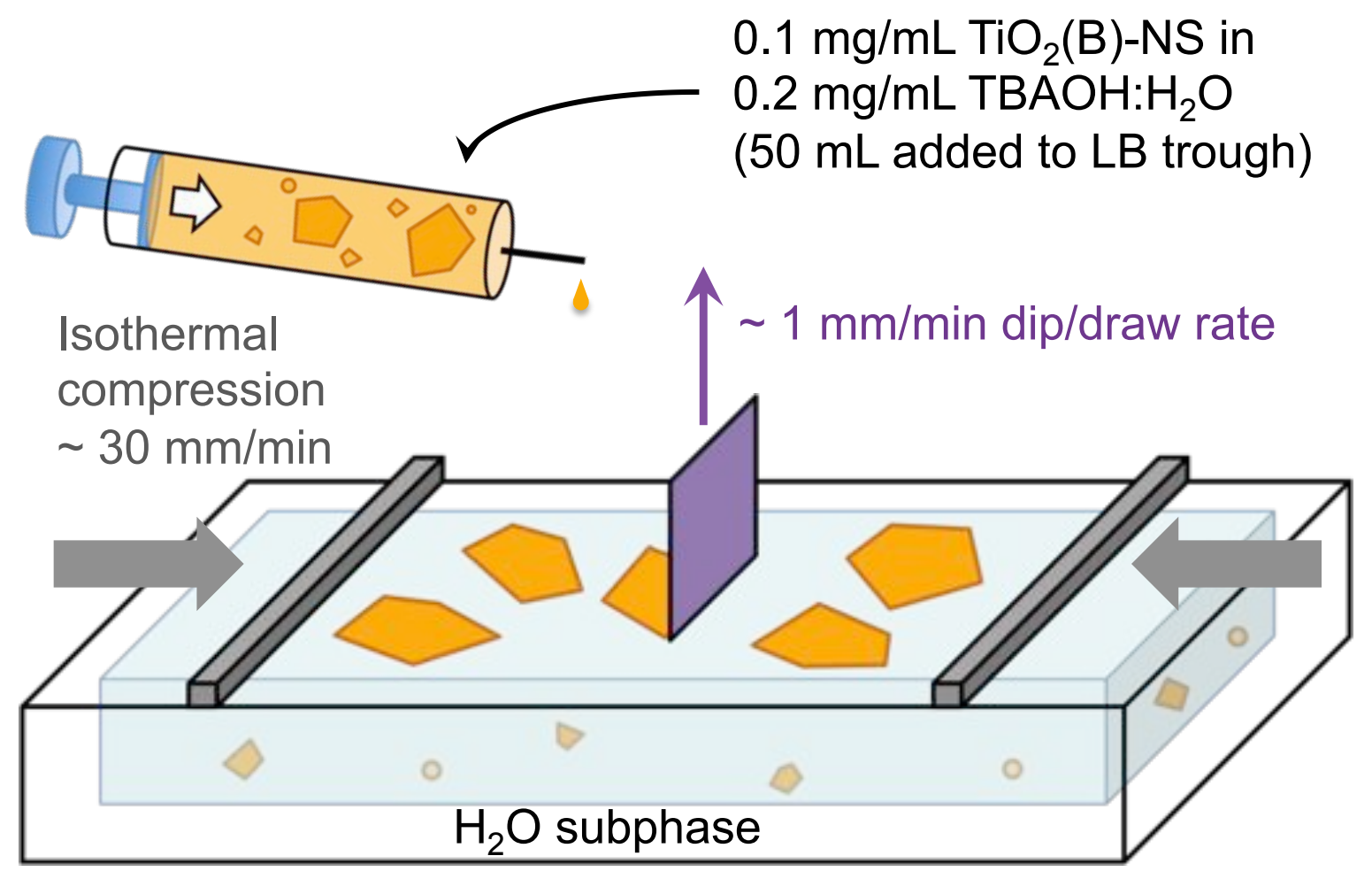
TiO_2(B) Nanosheets

- TiO_2(B) nanosheets [TiO_2(B)-NS] are particularly interesting.
  - Unique, broad lithiation behavior.
  - Potentially facile and stable lithiation.
  - Lattice relaxation predicted with DFT+U.
  - Dominated by surface pseudocapacitance.
  - Promising substrate for LEEM/PEEM studies.
- Drop casting of TiO_2(B)-NS from solution.
  - TiO_2(B)-NS suspended in ethanol, dropped by pipette onto substrate and air-dried.
  - Results in sparse films with significant particle agglomeration; some protrusion of flat sheets.
  - **Not suitable for LEEM/PEEM studies.**



Reference: Dylla, Xiao, Henkelman, and Stevenson, *J. Phys. Chem. Lett.* 2012, **3**, 2015–2019.

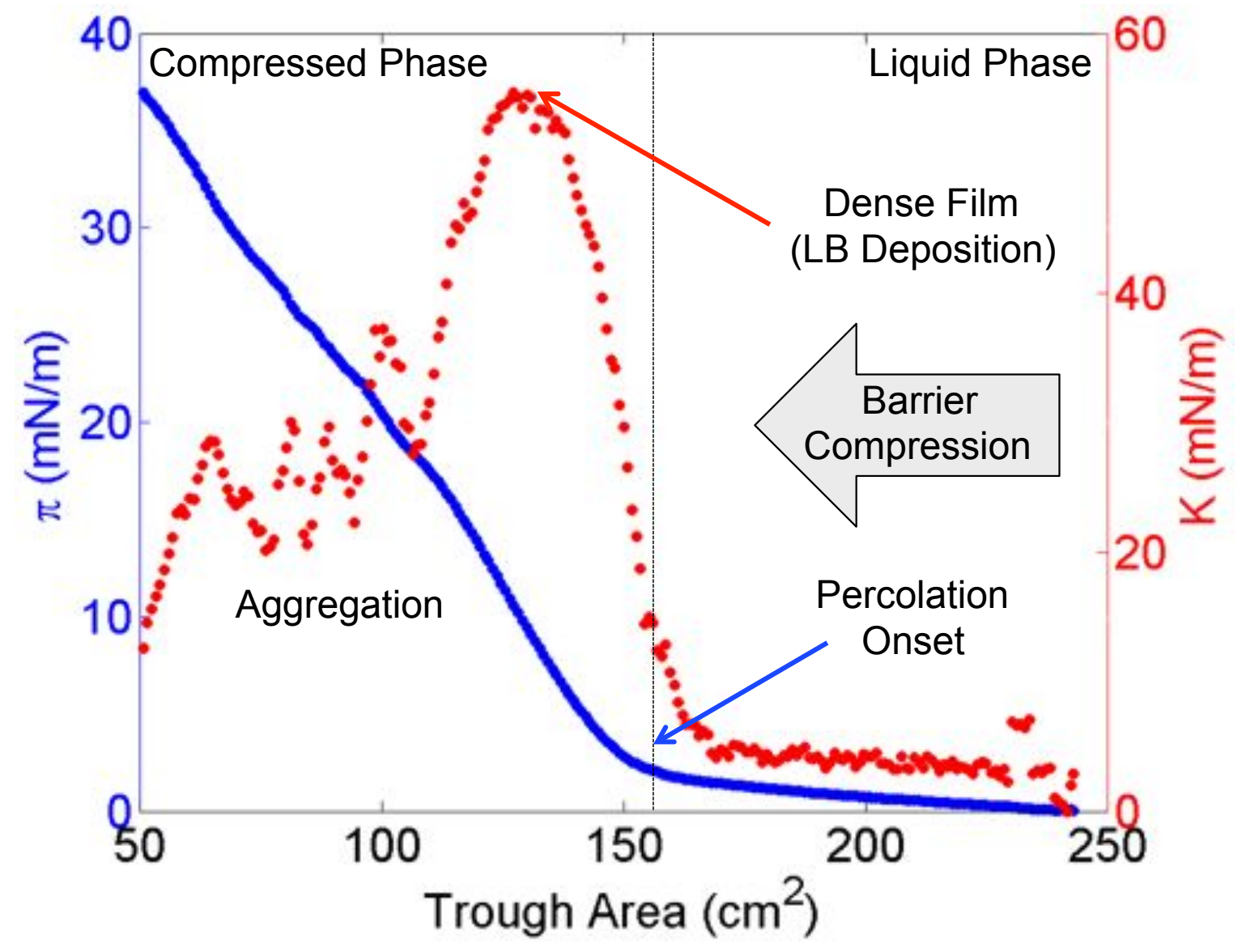
Langmuir-Blodgett Deposition of TiO_2(B) Nanosheets

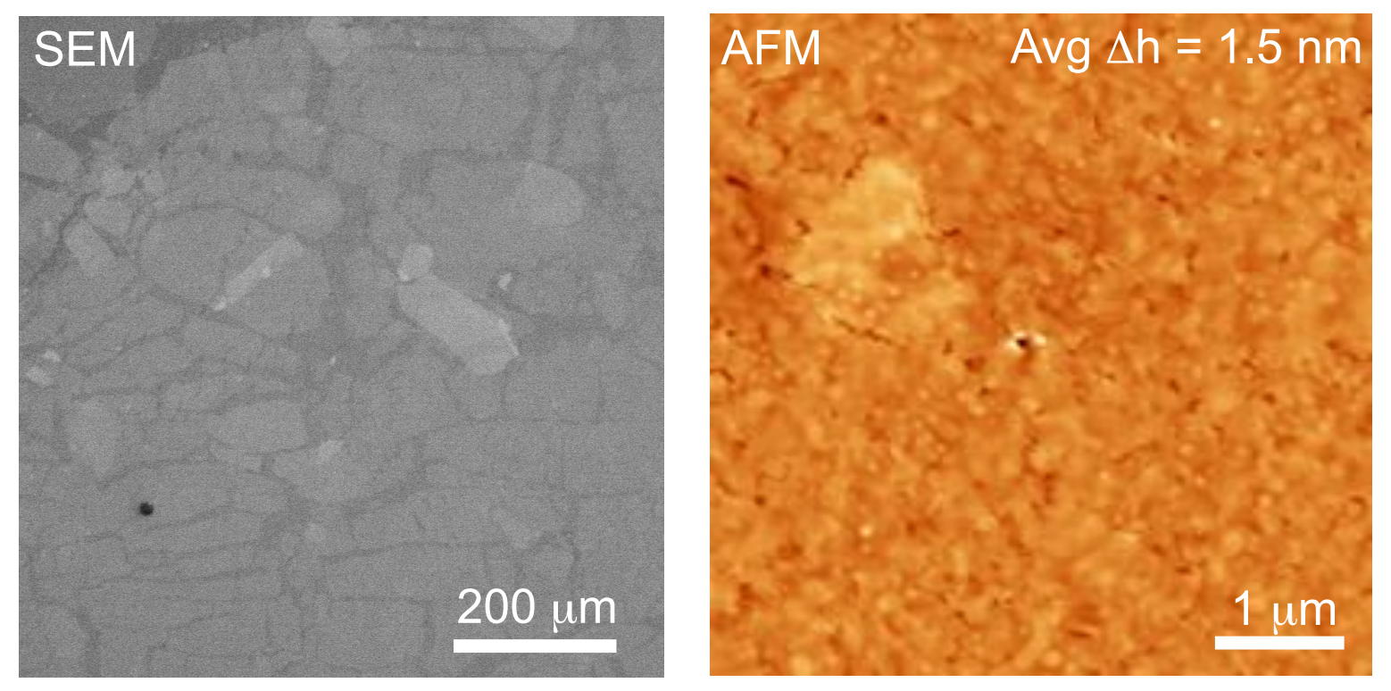


- Langmuir-Blodgett (LB) technique enables deposition of dense, ordered molecular monolayers on a variety of substrate types.
  - Well-known and well-characterized for amphiphilic molecules (e.g., biological materials).
  - Emerging technique for layering 2D nanosheets, e.g., graphene, graphene oxides, and titanates.
  - Used by Sasaki *et al.* to deposit $Ti_{1-\delta}O_2^{4\delta-}$ nanosheets exfoliated from bulk anatase and layered $Cs_{0.7}Ti_{1.825}\square_{0.175}O_4$ (□ = vacancy).
  - Results in amorphous and brookite-like NS.
- ***Our work: First demonstration of TiO_2(B)-NS deposited by Langmuir-Blodgett tehcnique.***
  - TiO_2(B)-NS synthesized by Dylla *et al.* (JPCL 2012).
  - TiO_2(B)-NS deposited by LB procedure above.
- Surface pressure (π) and compressibility (K) isotherms plotted versus trough area (A) for TiO_2(B)-NS on H_2O shown at right.
  - Increasing surface pressure indicates increasing TiO_2(B)-NS interactions with compression.
  - Compressibility calculated from surface pressure:

$$K = -A\frac{\partial \pi}{dA} \cong \frac{\pi_1 - \pi_2}{\ln A_1 - \ln A_2}$$

  - Maximum K indicates onset of dense film, decreasing K indicates yielding or aggregation.
  - Dip SiO_2/Si, hydrophobic and hydrophilic Au samples at maximum K for optimal LB deposition.
- **Preliminary SEM and AFM surveys at right indicate large continuous areas of conformal, densely packed nanosheets.**
  - Some multilayer regions or edge overlaps likely.



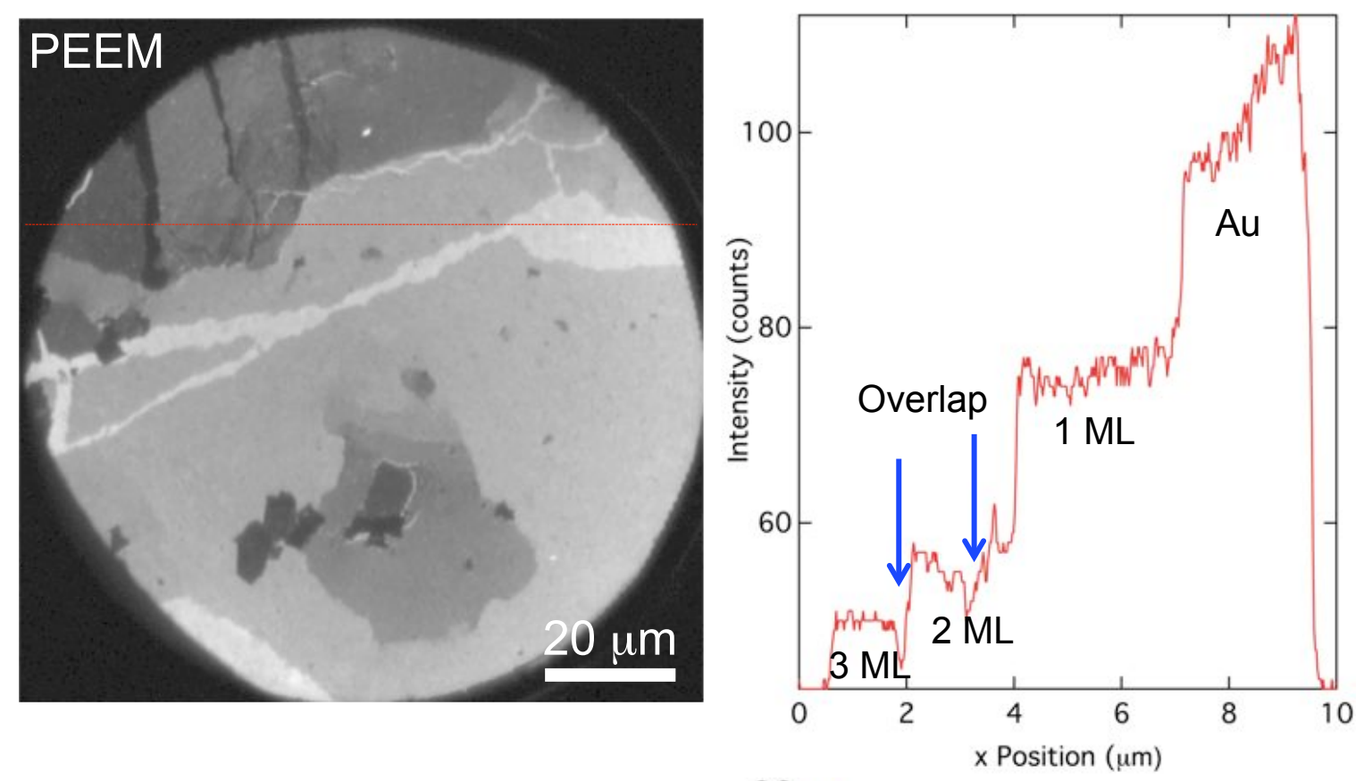


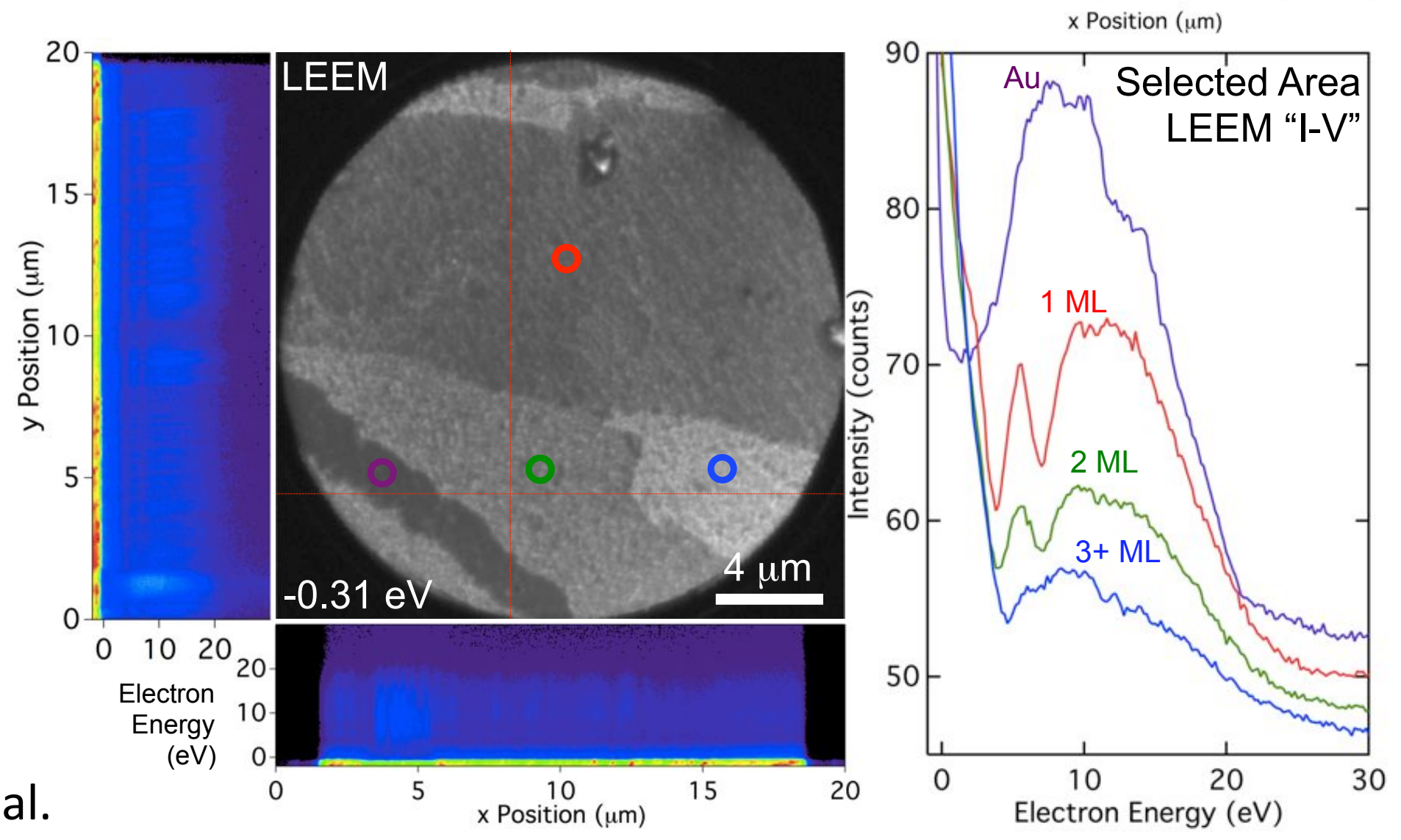
References: Muramatsu et al., *Langmuir* 2005, 21, 6590-6595; Dylla et al., *J. Phys. Chem. Lett.* 2012, **3**, 2015-2019; Reference: : L. Imperali et al., Langmuir 2012 ,28, 7990-8000.

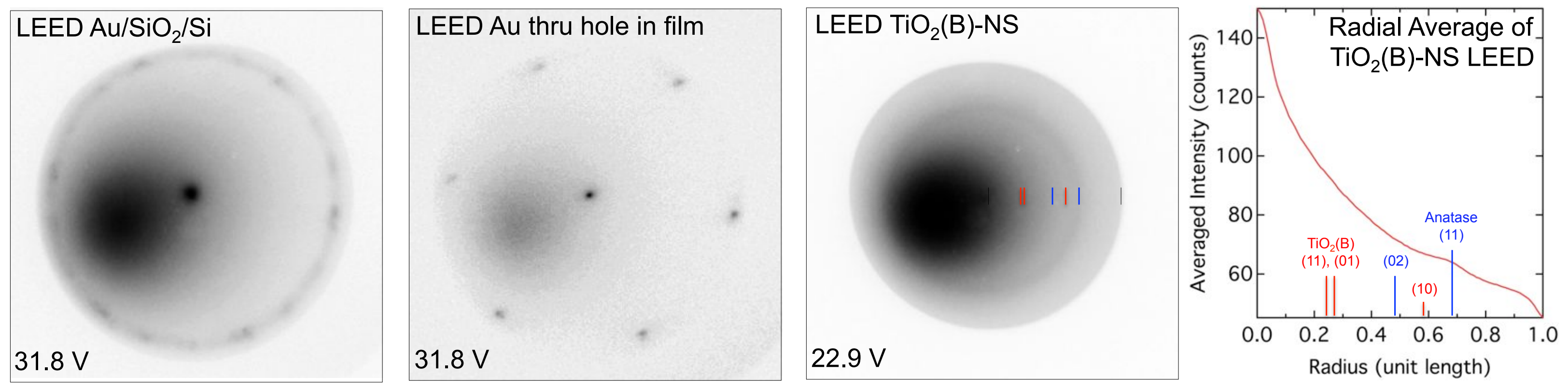
Properties of LB-Deposited TiO_2(B)-NS

Physical Properties Determined by LEEM, PEEM, and LEED

- **PEEM** shows large areas of densely packed nanosheets, with better contrast than SEM.
  - TiO_2(B)-NS absorb photoelectrons emitted by Au.
  - **Plateaus in the line profile indicate discrete layers.**
  - Dips in the line profile indicate areas of film overlap.
- **LEEM** shows at least four distinct regions.
  - Electron reflectivity image at -0.31 eV is related to topology, where brighter regions are higher.
  - Each region has a distinct LEEM "I-V" spectra, which are associated with Au, 1ML, 2ML, and 3+ ML of TiO_2(B)-NS.
  - **TiO_2(B)-NS show a resonance at 5.5 eV (λ_b = 3.78 Å) ⇒ related to d-spacing?**
  - Peak attenuation in thicker regions.
- **LEED** (below) highlights crystallographic properties of the LB-deposited TiO_2(B)-NS.
  - Local area LEED with 0.5 μm aperture.
  - Substrate is nanocrystalline Au(111).
  - Holes in the TiO_2(B)-NS film are mostly smaller than the size of an Au nanocrystal.
  - **TiO_2(B)-NS crystalline domains are less than 0.5 μm, and have random rotation.**
  - Due to poor diffraction conditions, crystalline phases of the TiO_2-NS films are currently ambiguous. Preliminary analysis indicates **film is predominantly anatase, possibly with some TiO_2(B) phases.**
    - H_2O is hypothesized to transform the kinetic TiO_2(B) phase into the stable kinetic anatase phase.
    - Better LEED data is required.







Conclusions and Future Work

Conclusions

- Large continuous areas of densely packed TiO_2-NS were deposited by LB technique.
- Films had discrete thicknesses of 1-3+ ML.
- TiO_2-NS deposited from water was largely anatase, with some TiO_2(B) phase possible.

Future Work

- Minimize phase transformation using non-aqueous subphase for LB-deposition.
- Improve quality of LEED images.
- Perform *in situ* real-time lithiation studies on TiO_2(B) and anatase nanosheets.

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