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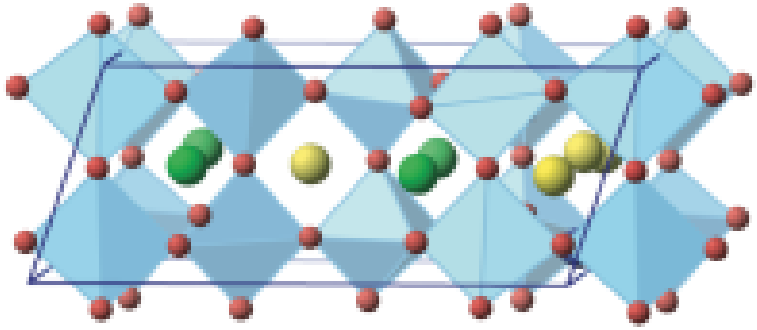
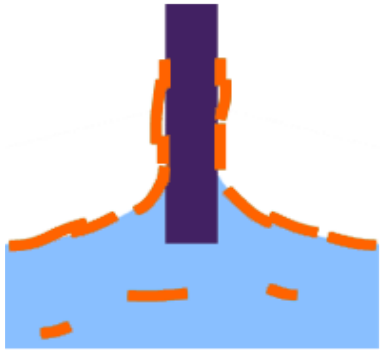
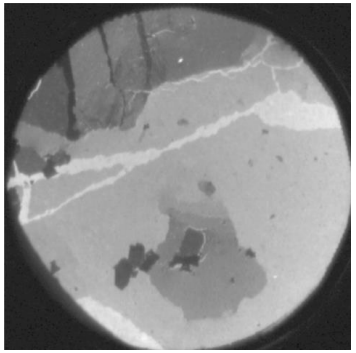
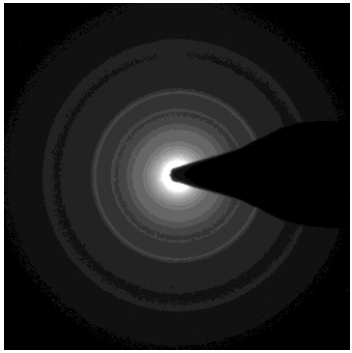
SAND2014-1720C









Polycrystalline TiO_2(B) Nanosheet Films Deposited via Langmuir-Blodgett Method

Laura Biedermann, Paul Kotula, Thomas Beechem, and Calvin Chan

Sandia National Laboratories, Albuquerque, NM

Anthony Dylla and Keith Stevenson

Dept. of Chemistry and Biochemistry, the University of Texas at Austin

EFRC CST

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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TiO_2 anodes have high operating potentials; TiO_2(B) has the highest capacity

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Nanostructured TiO_2 Compared to Graphite Electrode

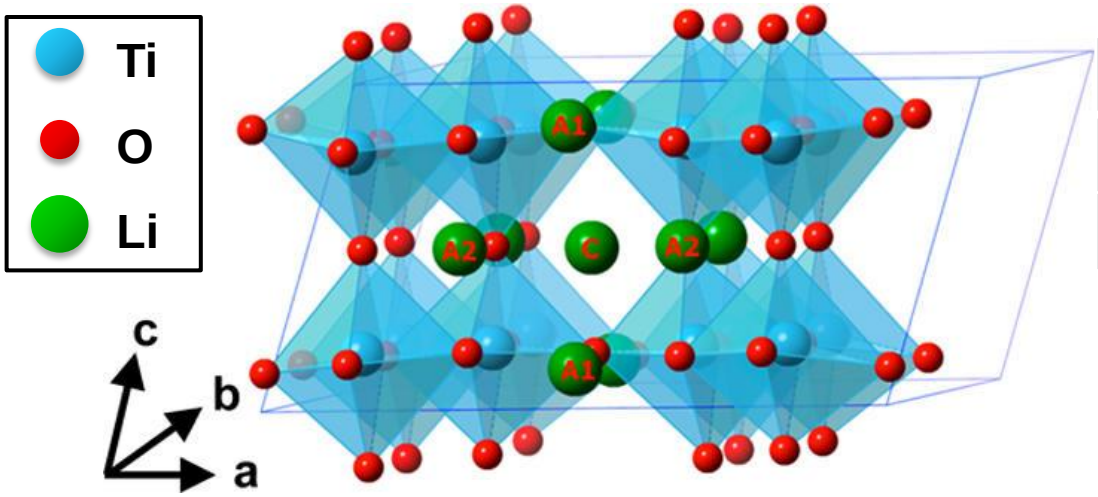
Higher operating potentials
⇒ **Safety**

Higher capacity at high (dis)charge rates
⇒ **Performance**

Lower solid-electrolyte interactions
⇒ **Degradation**

Lower volume change with lithiation
⇒ **Lifetime**

Unit cell of TiO_2(B) with idealized Li+ insertion sites [1]



Polymorph	Bulk	Nano
TiO_2(B)	0.85 Li^+/Ti	**1.0 Li^+/Ti**
Anatase	0.5 Li^+/Ti	0.85 Li^+/Ti

[1] Dylla *et al. J. Phys. Chem. Lett.*, (2012)

Nanostructured electrode materials allow for faster Li kinetics and greater capacities

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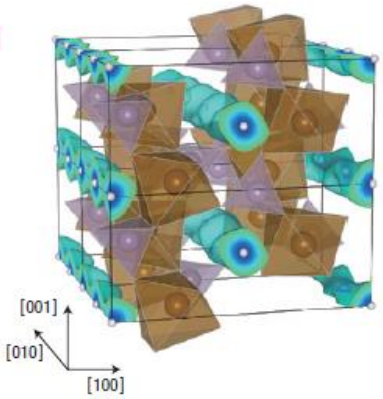
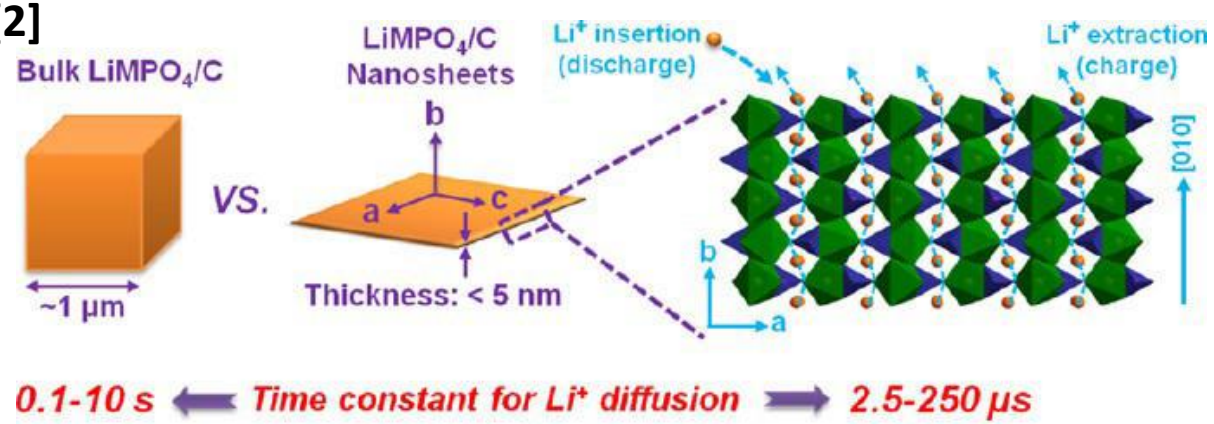
$LiMPO_4$ nanosheets demonstrate increased capacitance and capacity retention

[1]

$Li_{0.6}FePO_4$



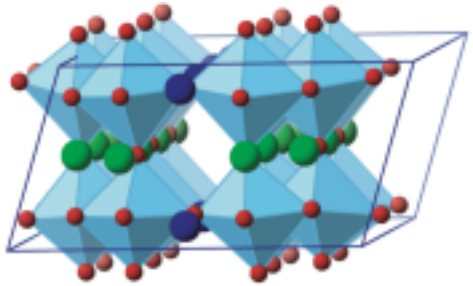
[2]



TiO_2(B): Nanostructure defines (de)lithiation pathways [3]

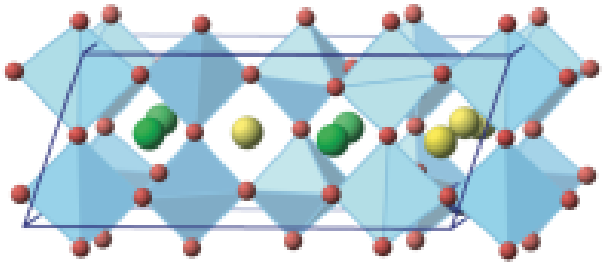
TiO_2(B) Nanoparticles

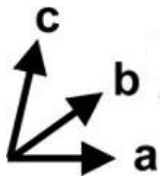
259 mAh/g



TiO_2(B) Nanosheets

275 mAh/g





[1] Nishimuri *et al., Nature Mater.* (2008); [2] Rui *et al., Nano Lett.,* (2013); [3] Dylla *et al. J. Phys. Chem. Lett.,* (2012)

Interfacial interactions are challenging to observe in TiO_2(B)-NS

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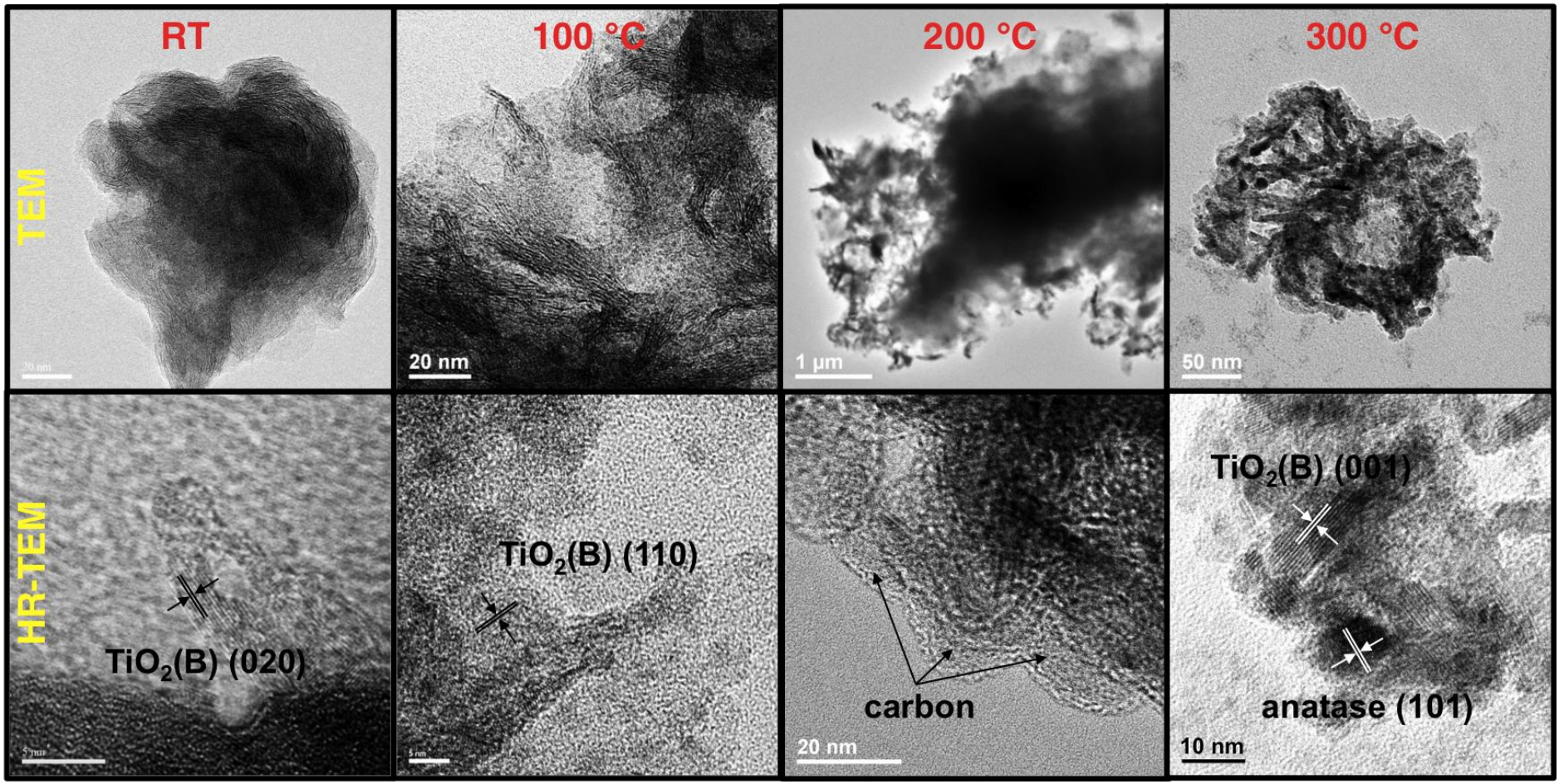
Phase transitions to anatase TiO_2 following heating in air atmosphere



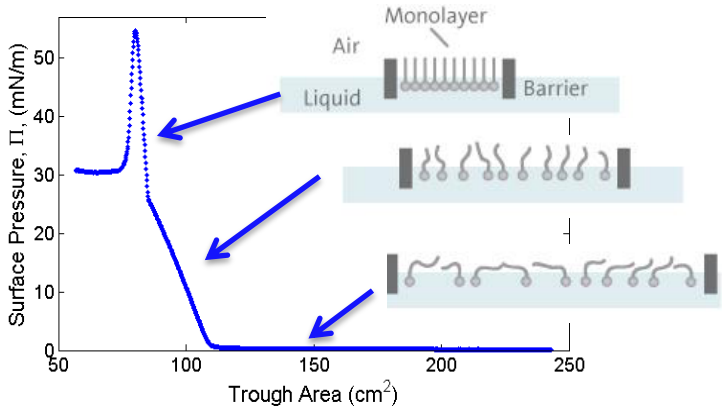
Dylla et al., "Electrochemical and Raman Spectroscopy Identification of Architectural and Morphological Transformations in Nanostructured TiO_2(B)." *submitted* (2013)

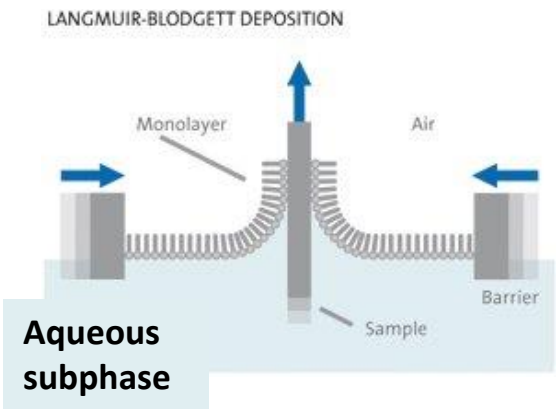
Laminar TiO2(B)-NS deposited via Langmuir-Blodgett deposition

Irving Langmuir

Katherine Blodgett

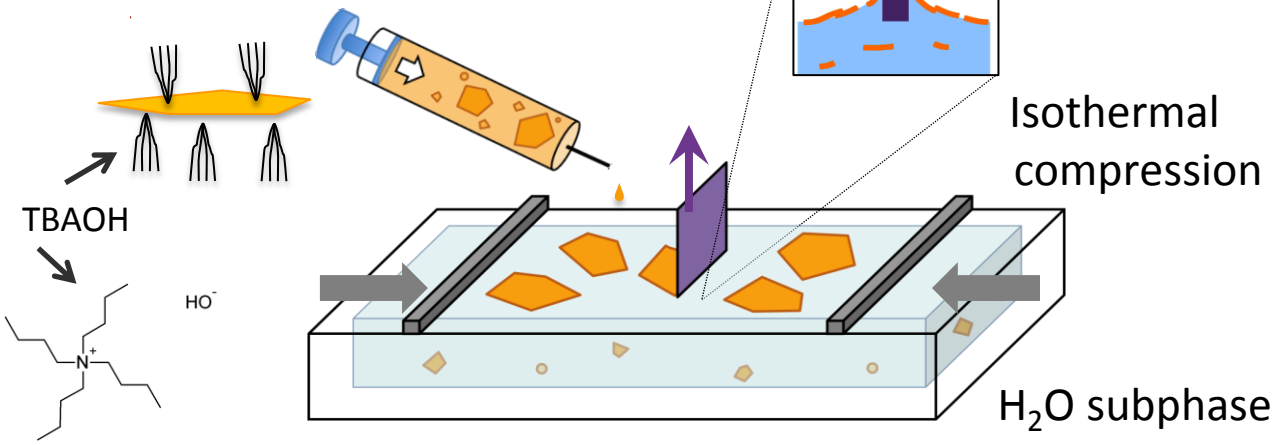
Compression of an amphiphilic molecule

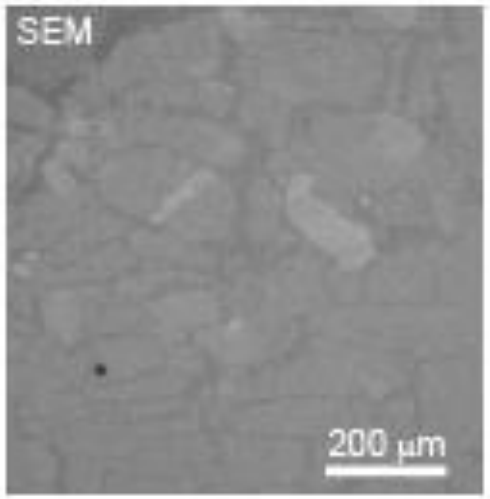




Amphiphilic surfactants allow deposition of oxide nanosheet monolayers

TiO_2(B)-NS in TBAOH:H_2O spreading solvent





TiO2(B)-NS assemble into large islands (>1 mm)

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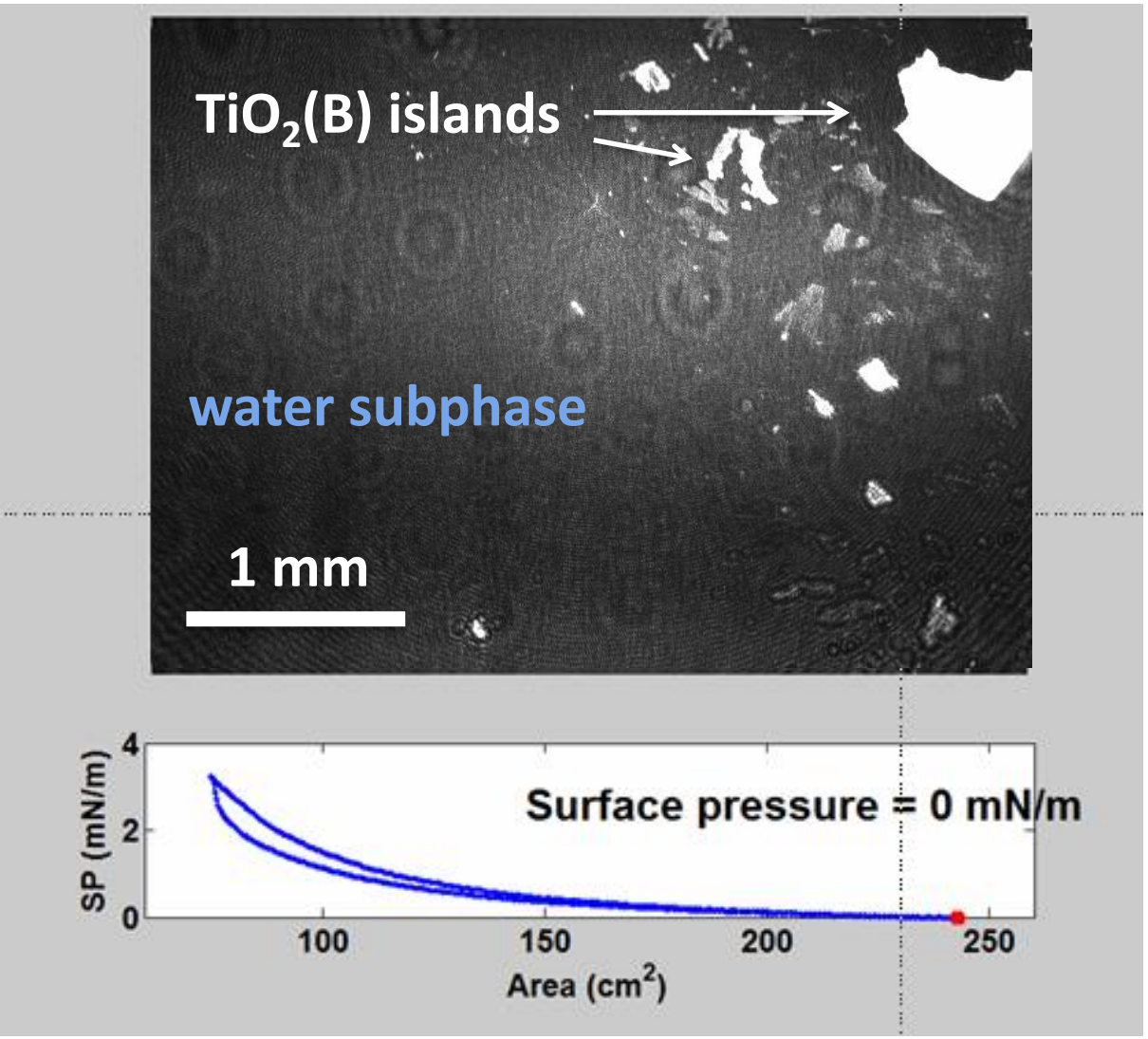

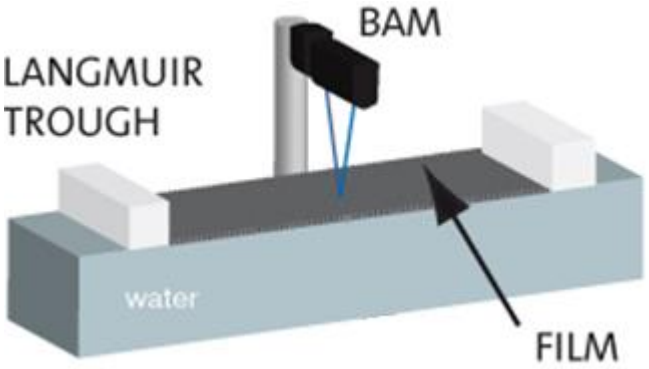

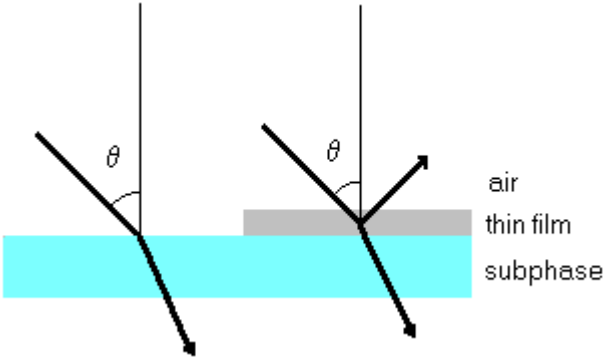

FOV: 4.0 mm x 3.6 mm; 12 µm resolution; 1 mm scale bar

TiO2(B)-NS assemble into large islands (>1 mm)

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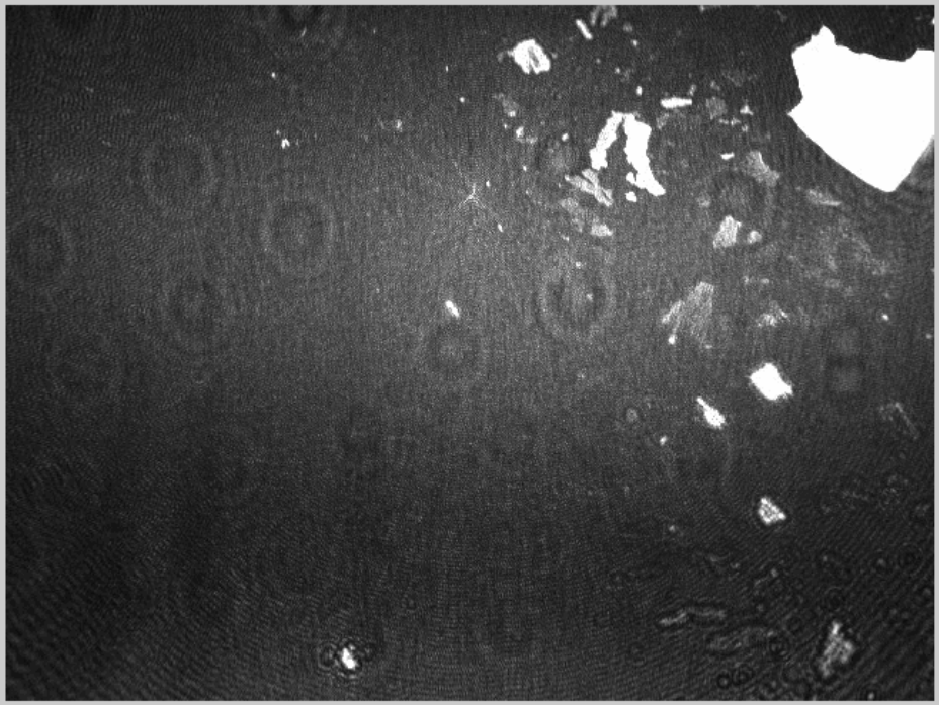
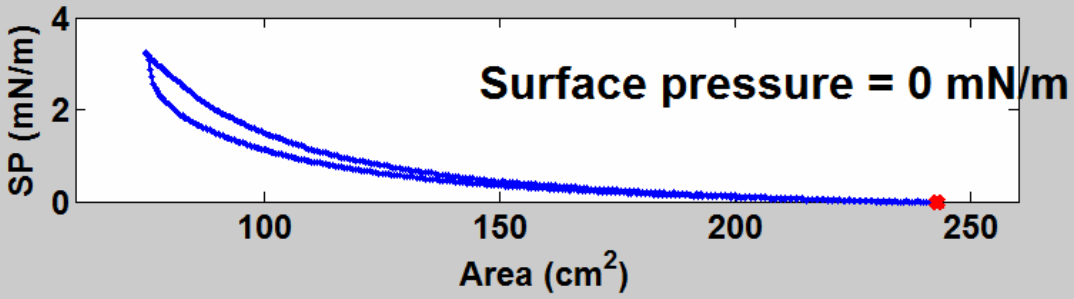
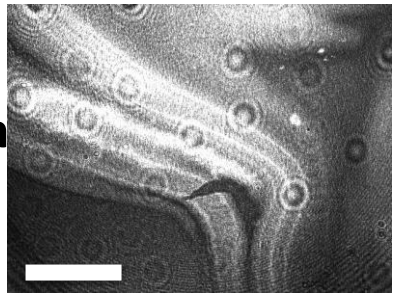
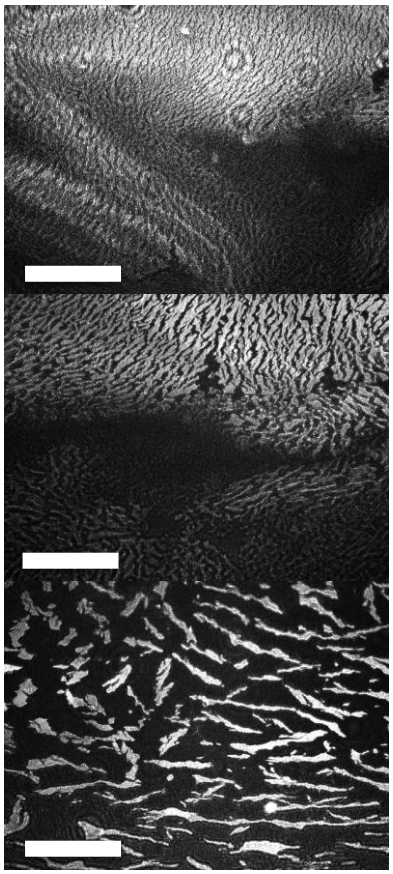




compression





expansion

FOV: 4.0 mm x 3.6 mm; 12 µm resolution; 1 mm scale bar

TEM confirms TiO_2(B) polymorph; nanocrystalline films

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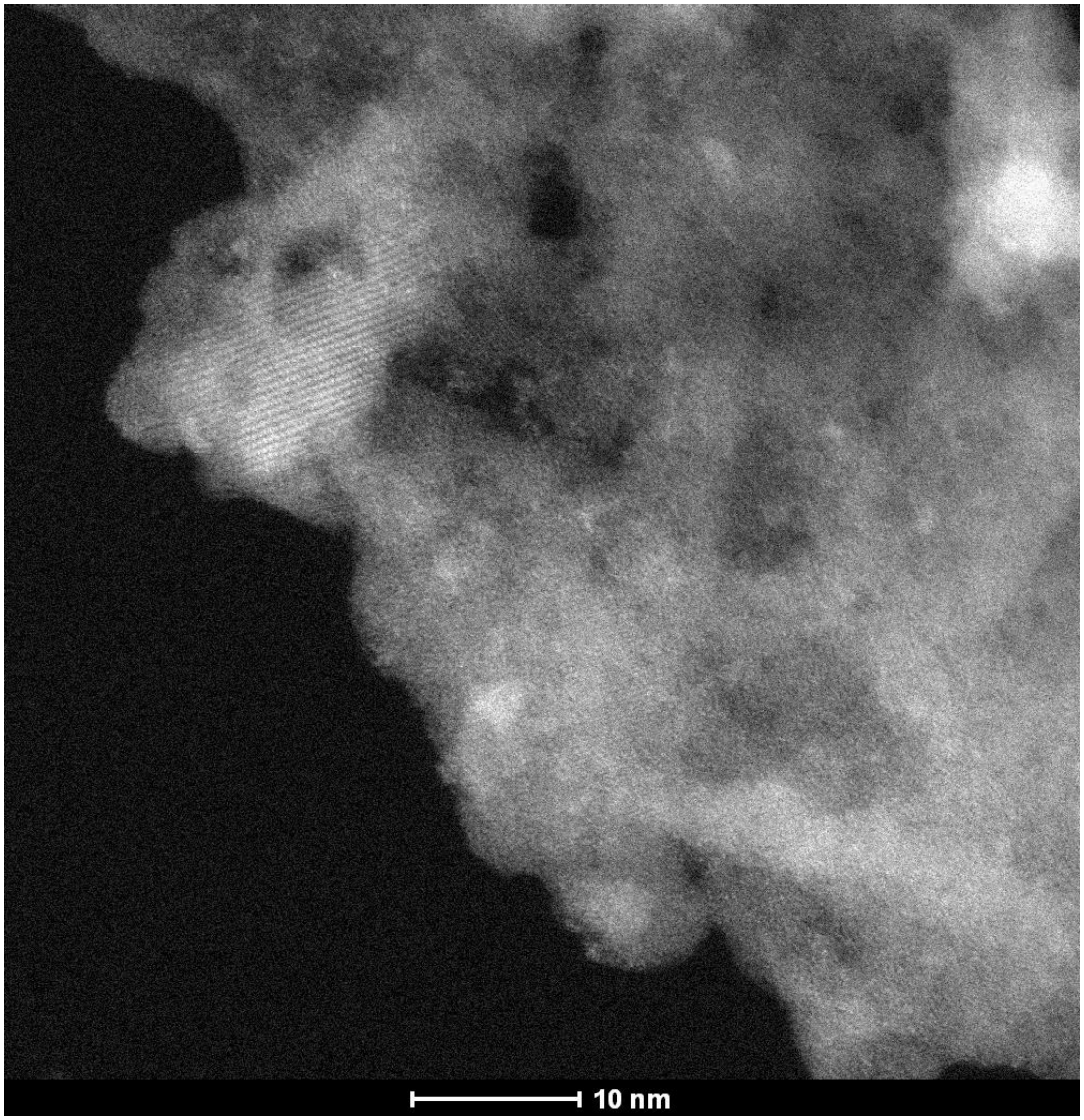
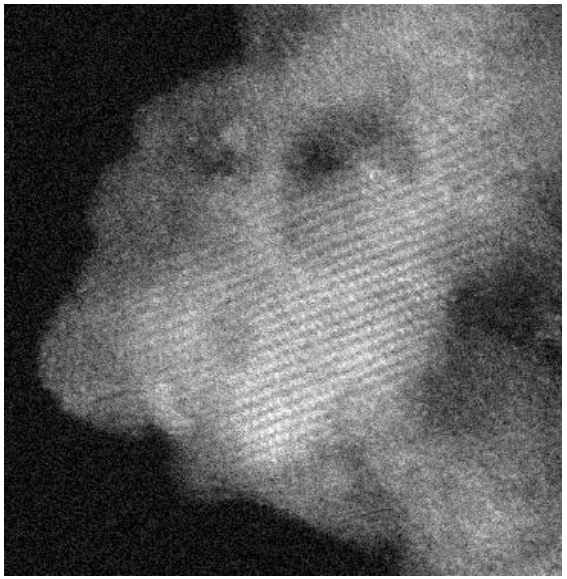
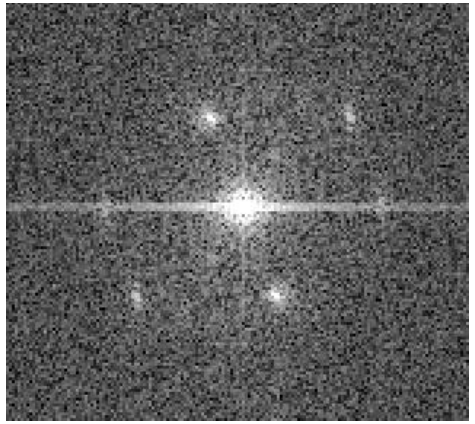
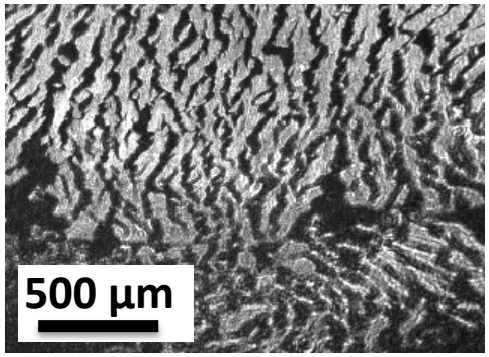
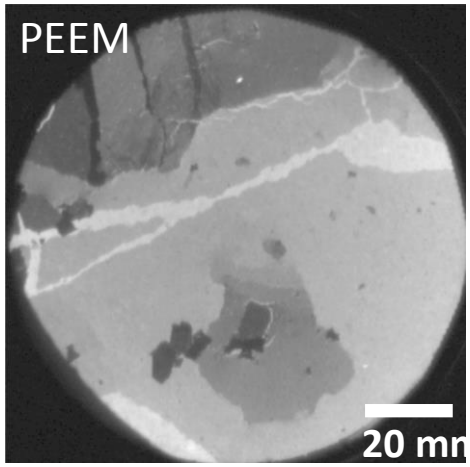






First observations of TiO_2(B)-NS as a monolayer material

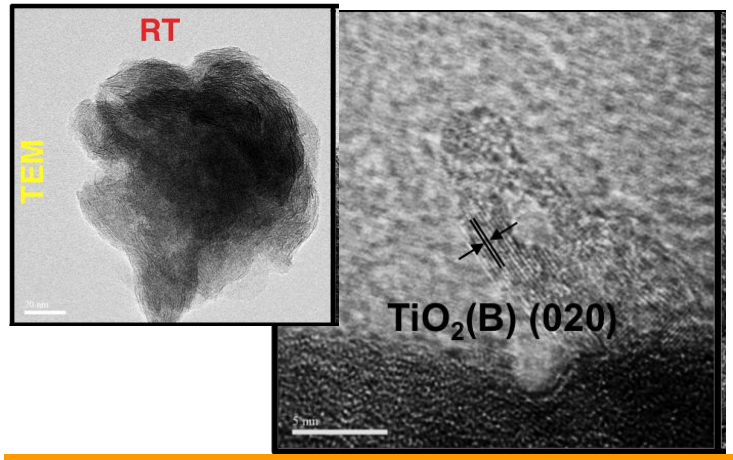


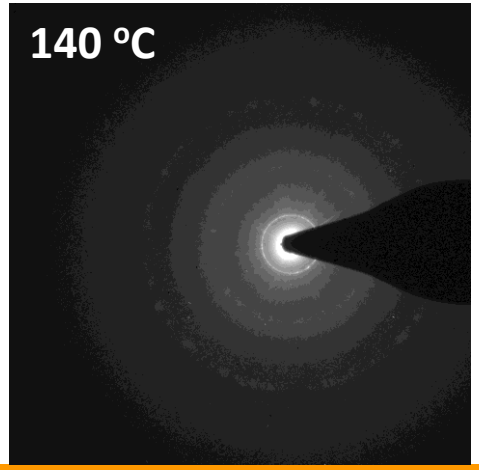


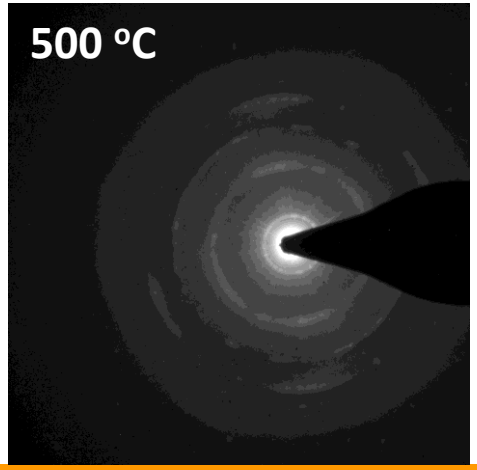
TiO_2(B) nanocrystals, ~10s nm across, comprise TiO_2(B) monolayers

PEEM: Photoelectron emission microscopy

TiO_2(B) nanosheets are phase-stable under heating to 500 °C in vacuum







Next step: In-situ observations of TiO_2(B)-NS lithiation

lbieder@sandia.gov

Acknowledgements

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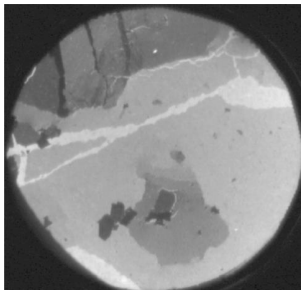
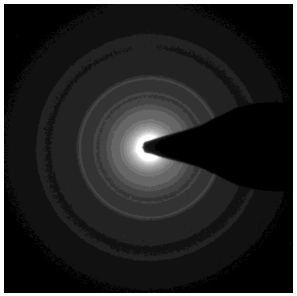
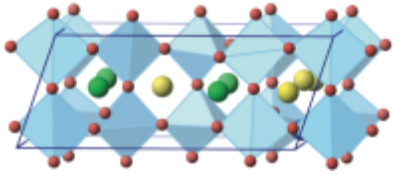
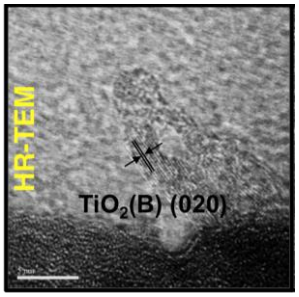




Calvin Chan, Paul Kotula, Thomas Beechem
G. Kellog, T. Ohta, C. Diaconescu, K. Zavadil, and K. Harrison

The University of Texas at Austin





Keith Stevenson, Anthony Dylla
G. Henkelman, P. Xiao, and J. Lee

U.S. DOE, Office of Science, BES
Energy Frontiers Research Center on
"Understanding Charge Separation and Transfer at Interfaces in Energy Materials (EFRC:CST)"
[Award DE- SC0001091]

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Langiappe

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Nanostructured TiO_2(B): Sheets vs. Particles

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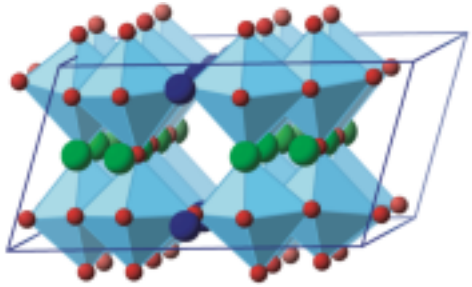
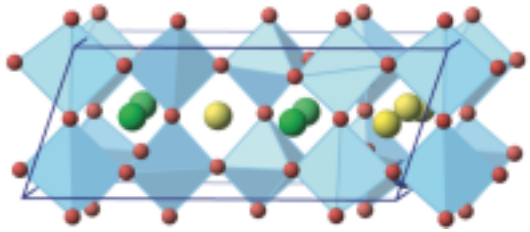
Lithiation Sites from DFT+U:

TiO_2(B) Nanoparticles

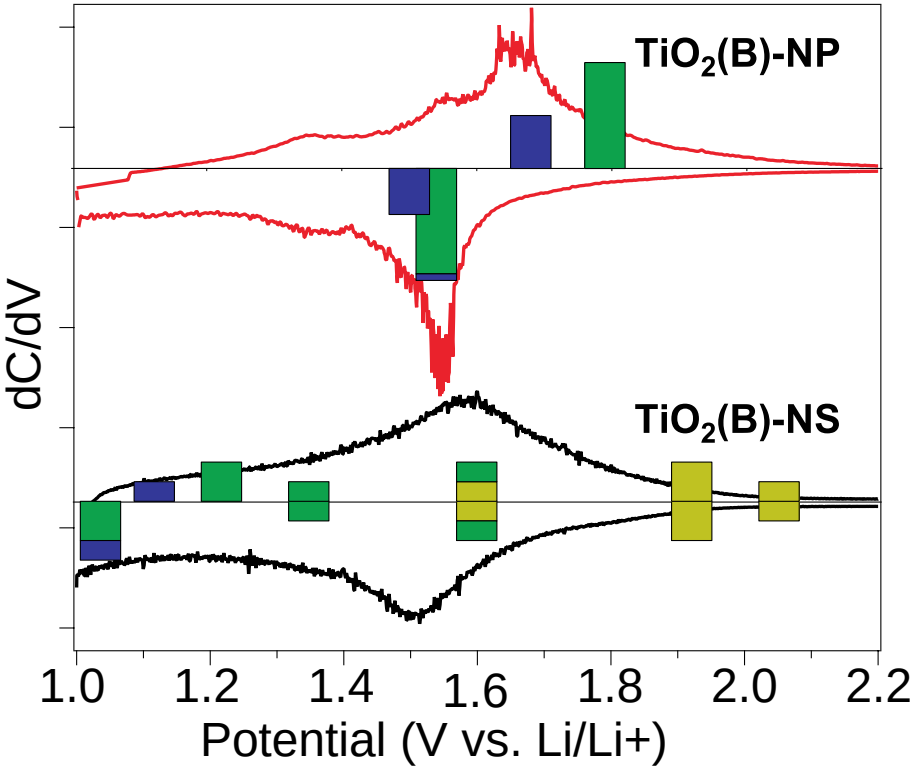


TiO_2(B) Nanosheets



C (x2 per unit cell)
A2 (x4 per unit cell)
A1 (x4 per unit cell)

Differential Capacity and DFT+U

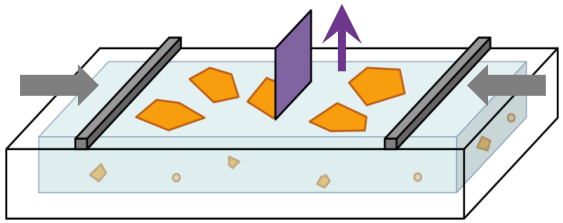


- **TiO_2(B)-NS:** Adjacent A2 sites in TiO_2(B)-NP merge and shifts away from C sites.
  - Li^+-Li^+ repulsion reduced ⇒ enables filling of energetically favorable C site.
  - Loss of e- sharing between adjacent Li^+ ⇒ decreases energy penalty for delithiation.
  - Potentially less irreversible capacity loss (ICL) ⇒ surface chemistry?

Dylla *et al. J. Phys. Chem. Lett.* **3**:2015 (2012)

LB Deposition of TiO_2(B)-NS

SEM of TiO_2(B)-NS LB-deposited on SiO_2.



$$e_{eq} = - A \frac{\P p}{dA}$$