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Developing a Platform for *in situ* Studies of Metal-Oxide/Carbon Systems

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DEPARTMENT OF ENERGY NEES NANOSTRUCTURES *for* ELECTRICAL ENERGY STORAGE

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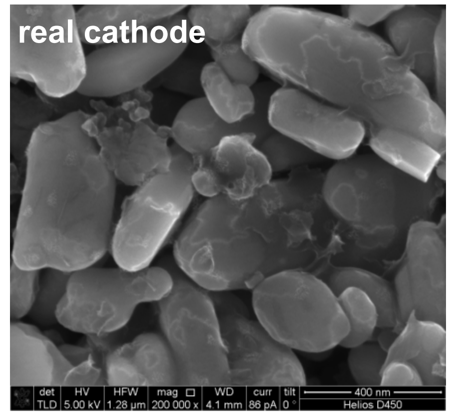
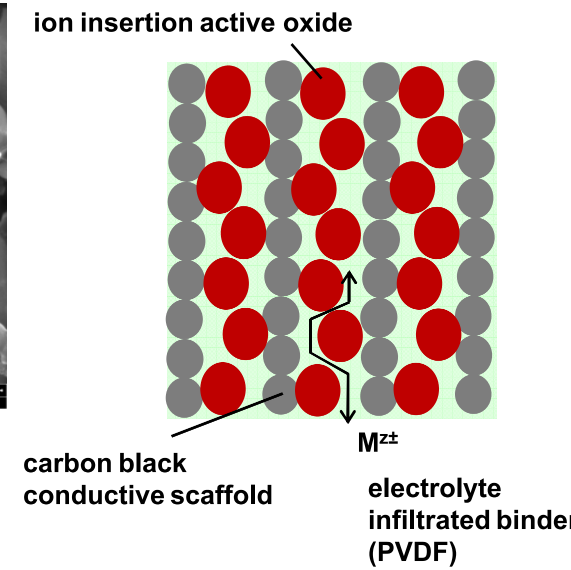
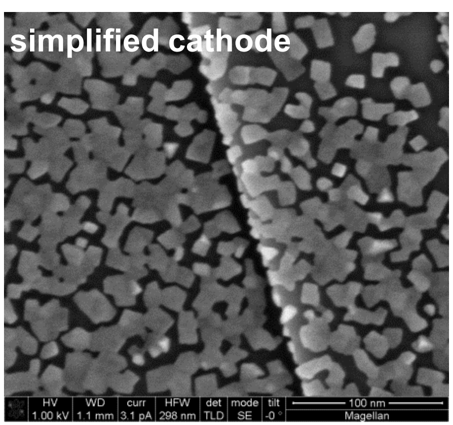
Reducing the dimensionality of composite electrodes

- ***Platform development:***
  - **Simplified metal-oxide/carbon electrode**
  - **Structure-activity relationships at the individual nanoparticle level, in situ**
- ***Application**:*
  - **Role of structure and interface in activity of β-MnO_2-graphite system using EC-AFM**

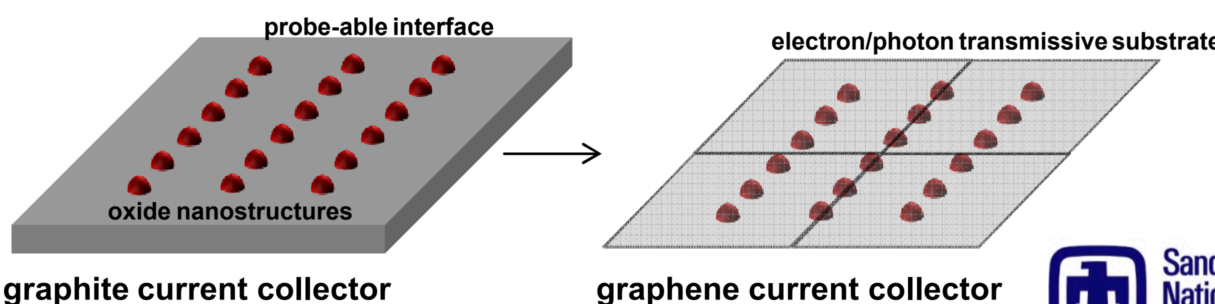


Positive electrode structure





Simplified positive electrode structures



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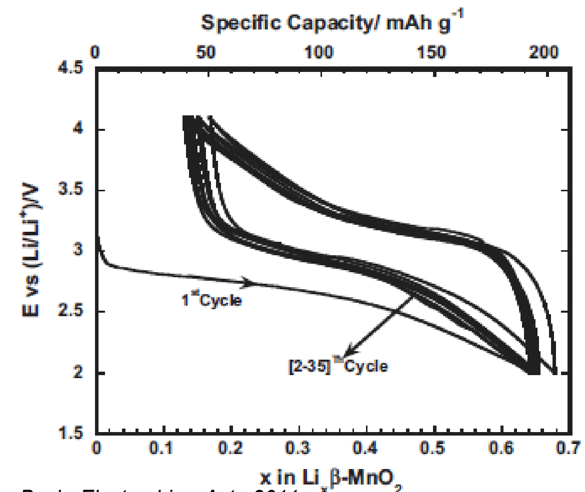
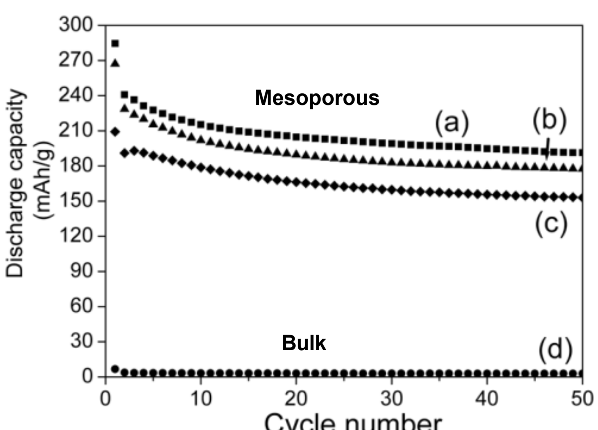
An active metal-oxide test case: β-MnO_2

- **Why β-MnO_2?**
  - Thermodynamically stable phase
  - Active cathode material for Li-insertion
  - Activity is size/structure dependent
  - **Li-insertion accompanied by substantial lattice change (16% for *a*)**



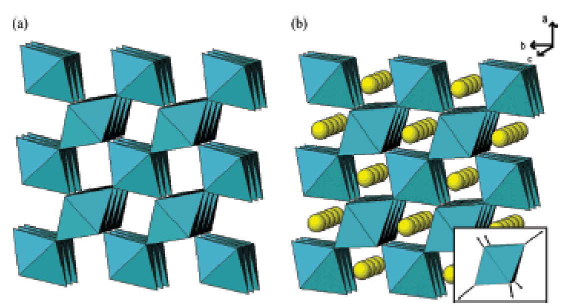
Bach, Electrochim. Acta 2011

Size/structure dependant activity



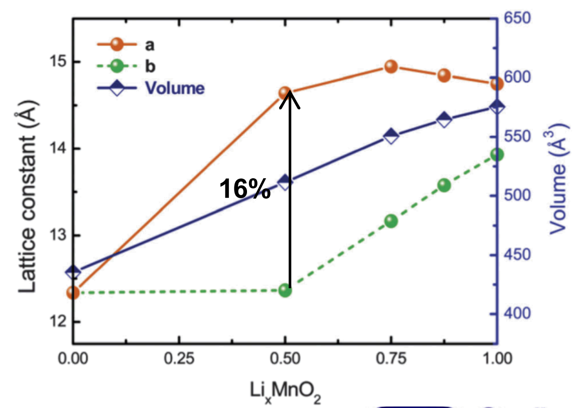
Bruce, Adv. Mater. 2007

(001) Li-insertion/transport



Bruce, JACS 2010

Structural signature of activity



Liu, PCCP 2013

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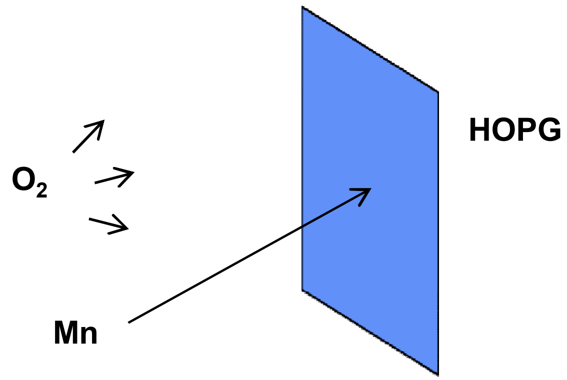
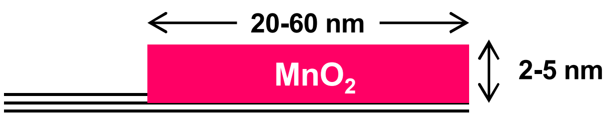
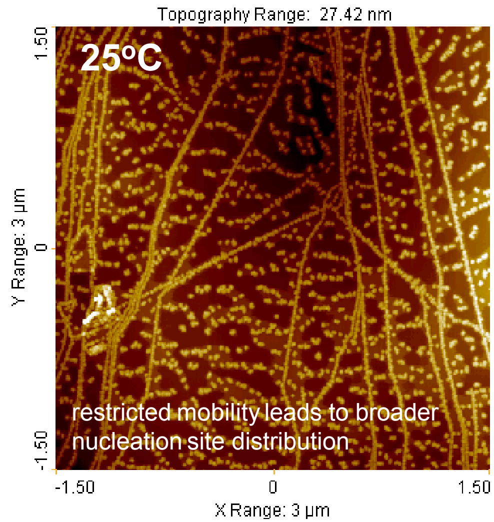
Directed β-MnO_2 nanostructure growth on graphite

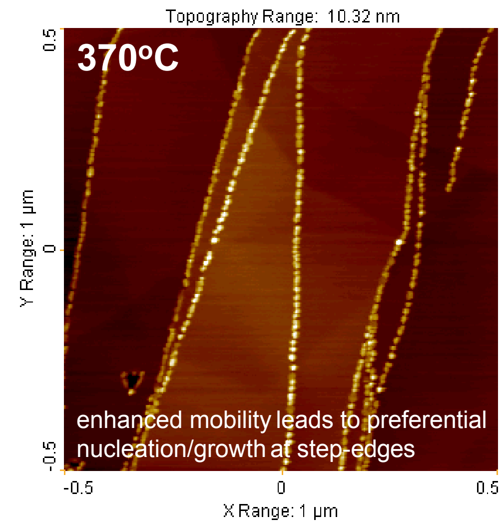
Low-flux metal oxide growth on carbon support



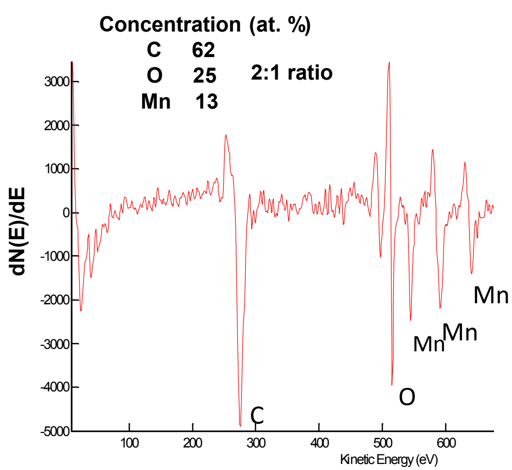


Island distribution governed by surface mobility.

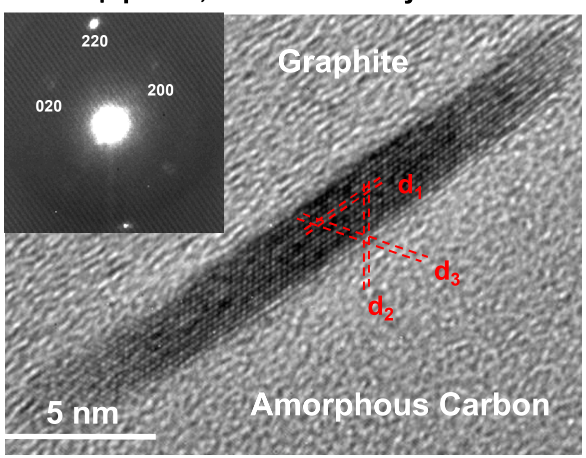




MnO_2 composition confirmed by Auger spectroscopy



High temperature growth yields thermodynamically stable β-phase, as confirmed by TEM



Tetragonal structure of β-MnO_2

a = 0.440 nm

c = 0.287 nm

β-MnO_2 islands exhibit substrate registration: c-axis in plane with HOPG terrace, *a* axis normal to surface

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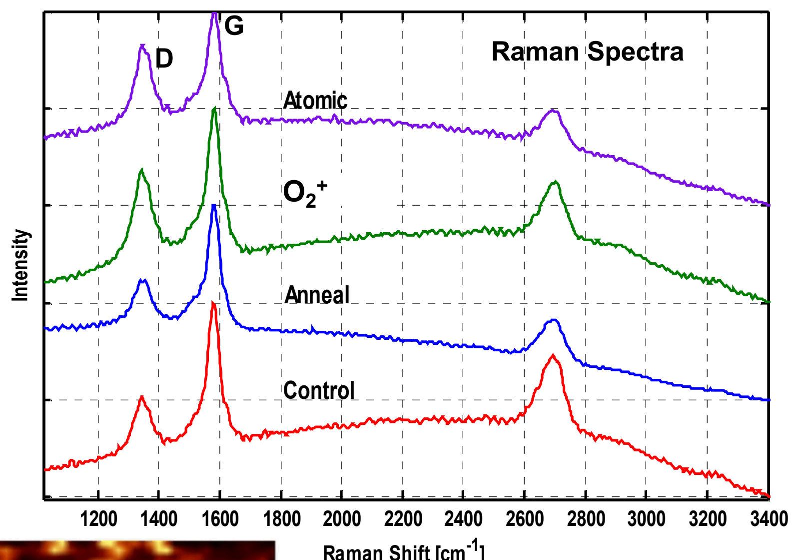
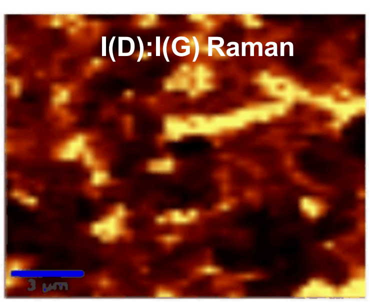
Controlling high temperature nucleation/growth via oxygen functionalization

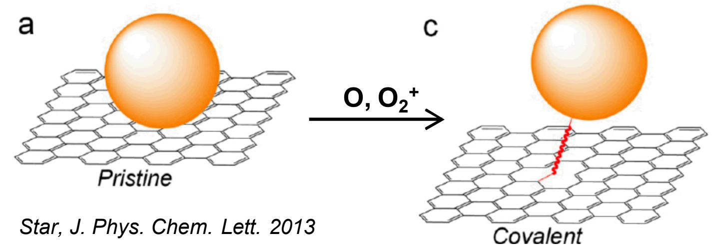
Oxygen functionalization routes:

- **Atomic oxygen: Mn deposition in O/O_2 background**
- **Ionic oxygen: O_2^+ irradiation prior to Mn deposition in O_2**



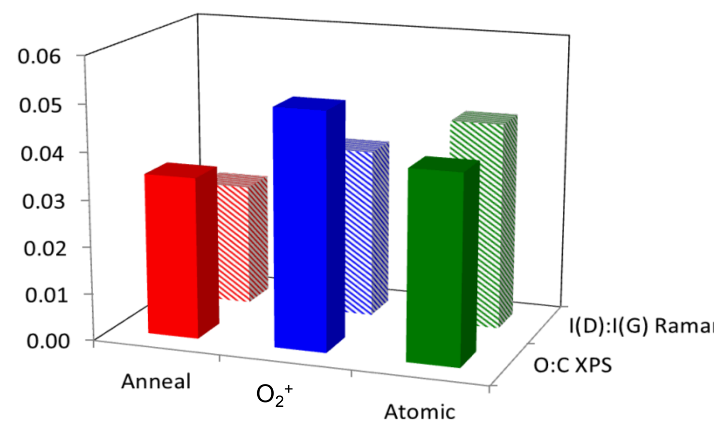


Generate oxygenated defects to act as covalent linkers



Star, J. Phys. Chem. Lett. 2013

XPS and Raman illustrate confirm perturbation of surface layers via increased disorder and oxidation



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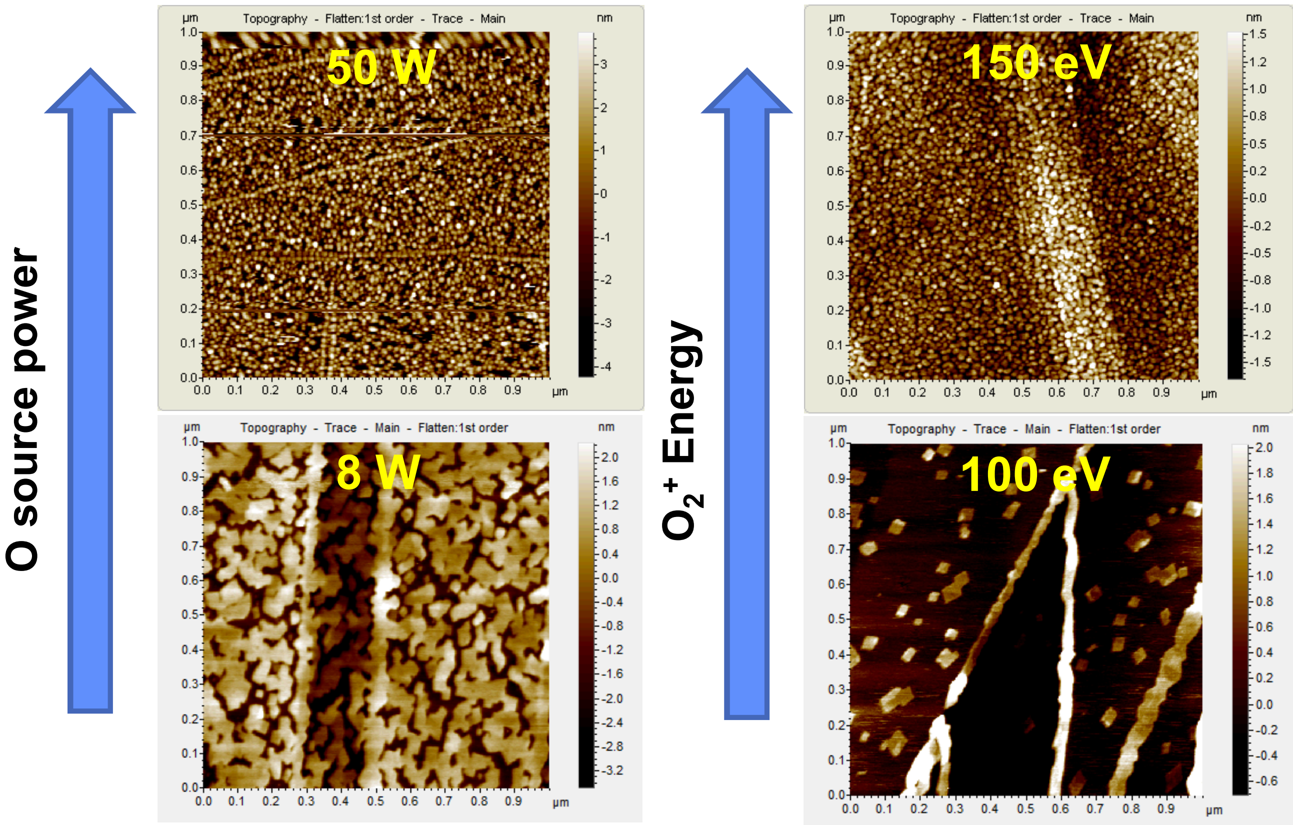
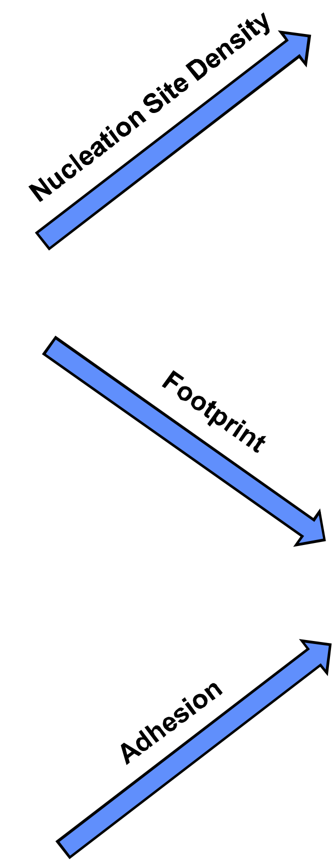
Functionalization controls particle size, number density, adhesion strength…

O Synthesis

O_2^+ Synthesis



Functionalization Trends



- **Tunable terrace structure size, packing density, adhesion strength**
- **Trade-off between particle isolation and adhesion**
- **Can grow isolated islands, semicontinuous films and continuous nanoribbons**
  - ***Can go after activity as a function of structural form and interface***

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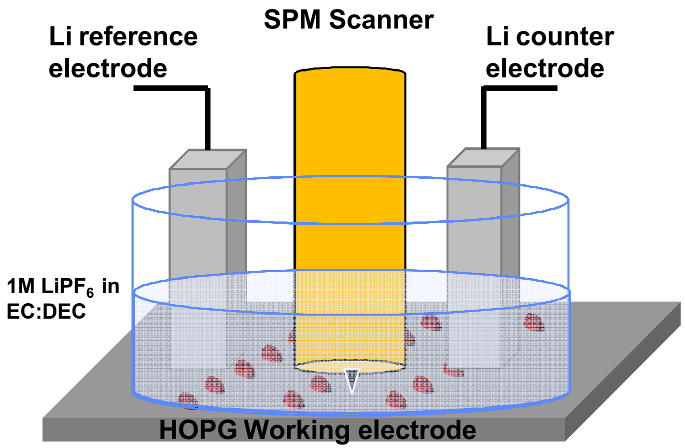
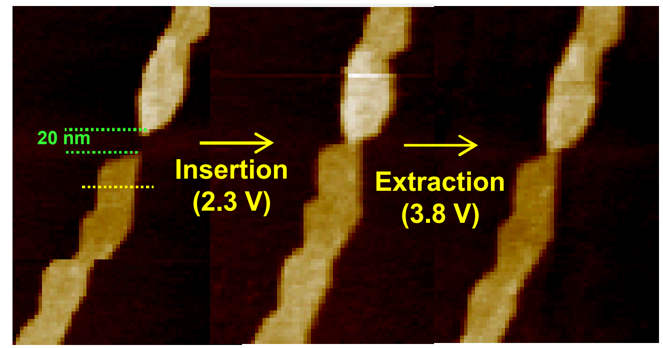
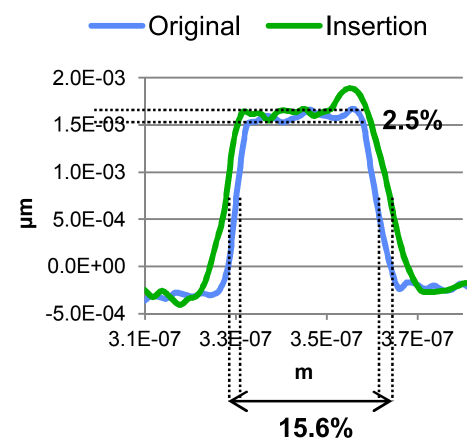
In-situ characterization of β-MnO_2 lithiation

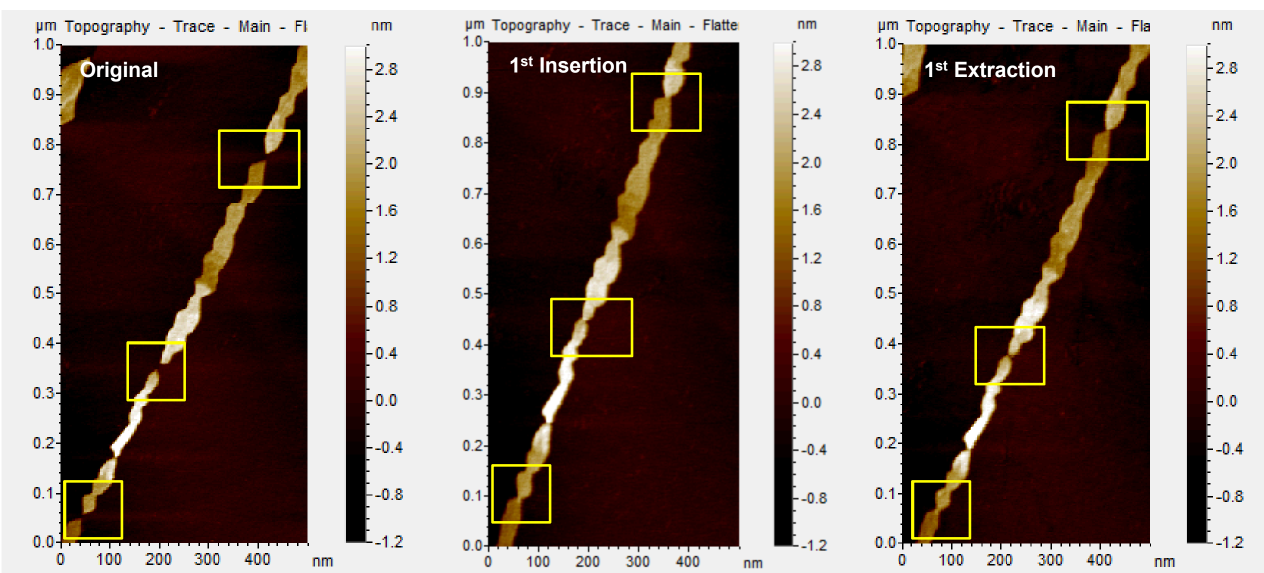
In-situ AFM provides information regarding particle lithiation and delithiation response



Nanoribbon expansion during first lithiation







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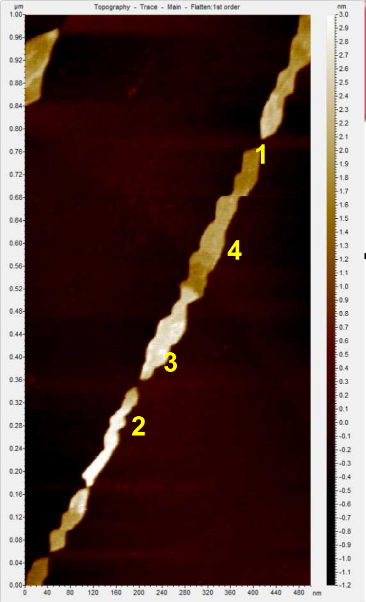
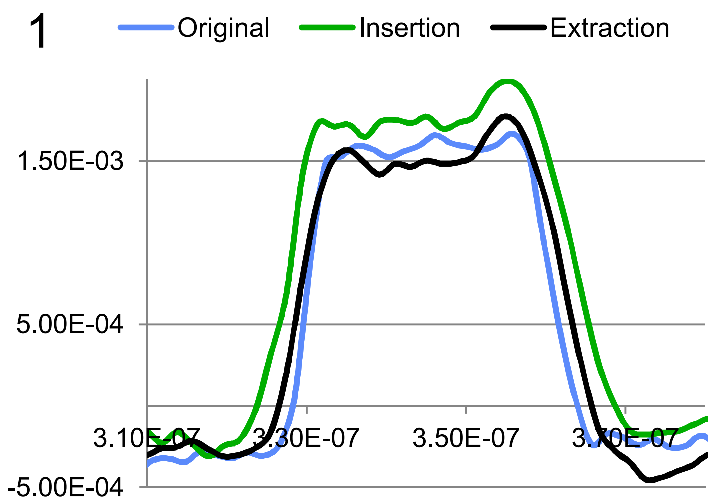
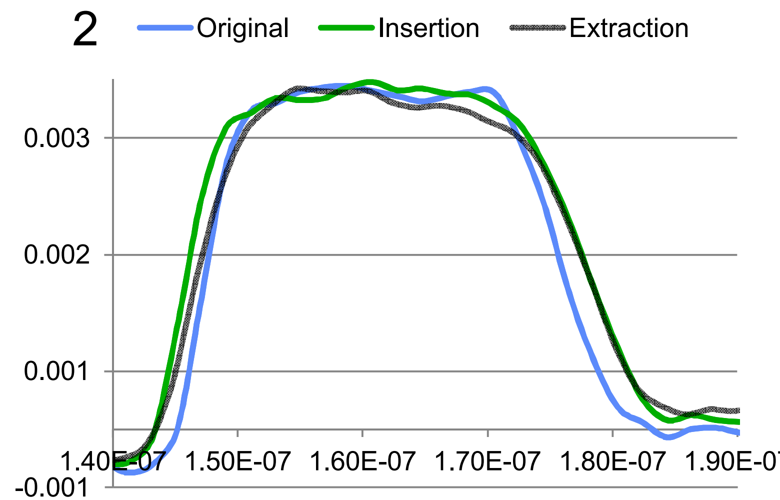
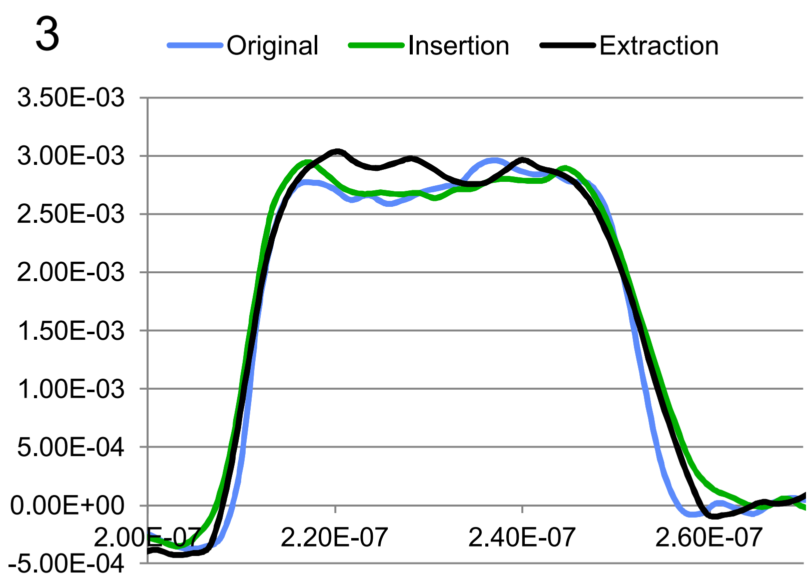
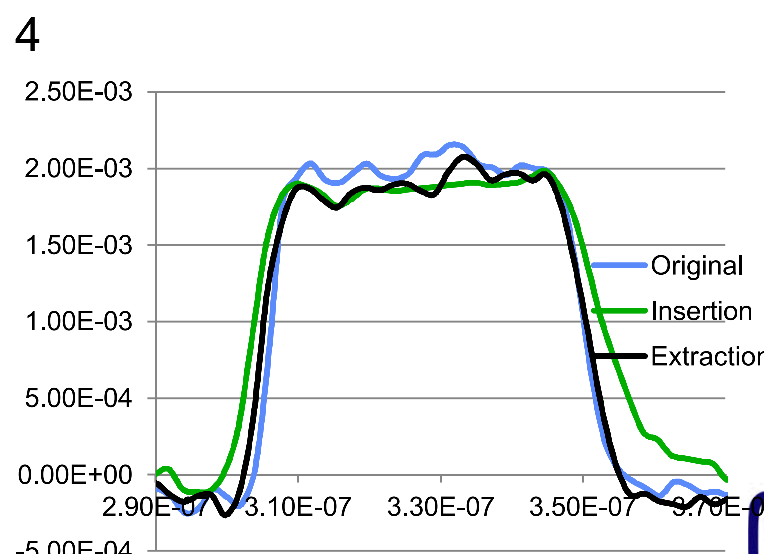

1
4
3
2


1
Original
Insertion
Extraction
1.50E-03
5.00E-04
-5.00E-04
3.10E-07
3.30E-07
3.50E-07
3.70E-07

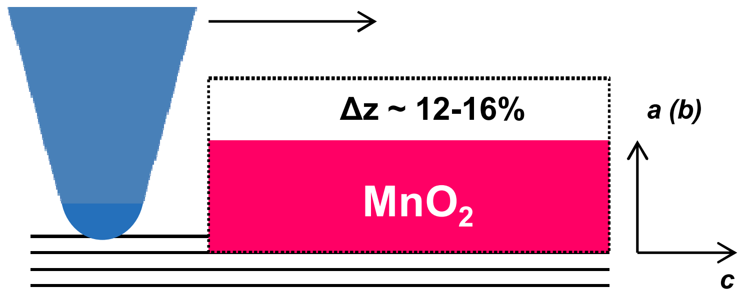

2
Original
Insertion
Extraction
0.003
0.002
0.001
-0.001
1.40E-07
1.50E-07
1.60E-07
1.70E-07
1.80E-07
1.90E-07


3
Original
Insertion
Extraction
3.50E-03
3.00E-03
2.50E-03
2.00E-03
1.50E-03
1.00E-03
5.00E-04
0.00E+00
-5.00E-04
2.00E-07
2.20E-07
2.40E-07
2.60E-07

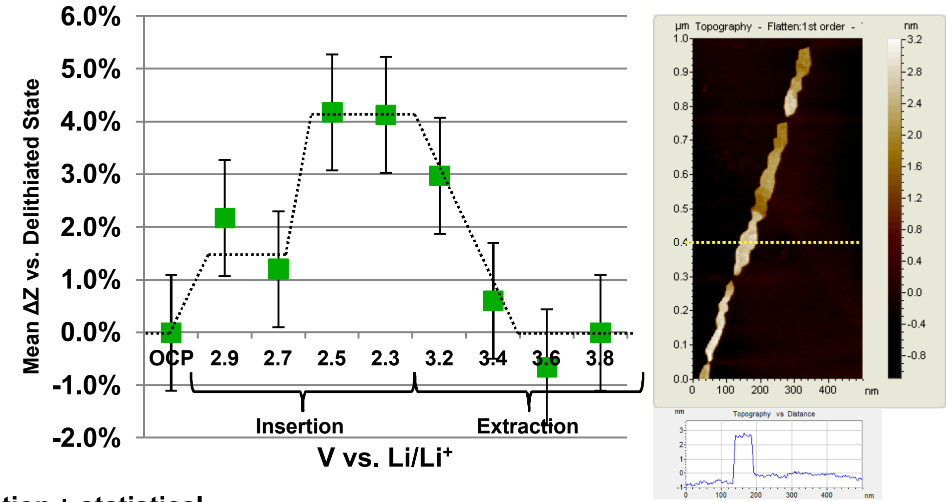

4
2.50E-03
2.00E-03
1.50E-03
1.00E-03
5.00E-04
0.00E+00
-5.00E-04
2.90E-07
3.10E-07
3.30E-07
3.50E-07
3.70E-07
Original
Insertion
Extraction

Quantifying particle/ribbon activity via lattice expansion

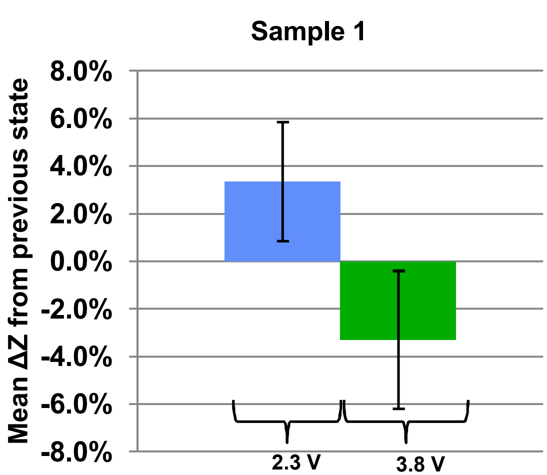
In-situ height measurement to detect *a/b* expansion:

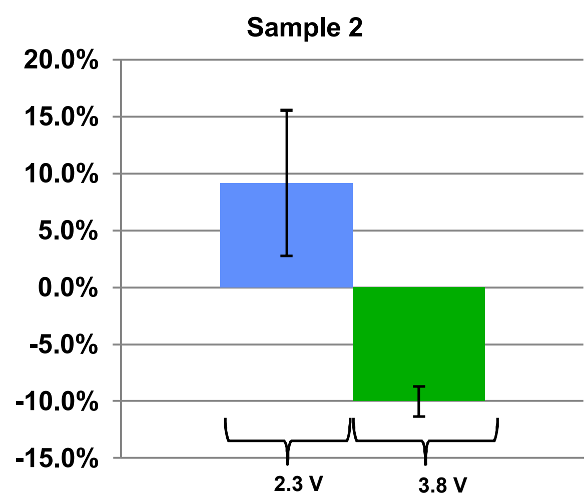


Potential dependent lithium insertion/extraction for step-edge β-MnO_2 nanoribbons



Potentiostatic switching experiments demonstrate large activity variation + statistical noise





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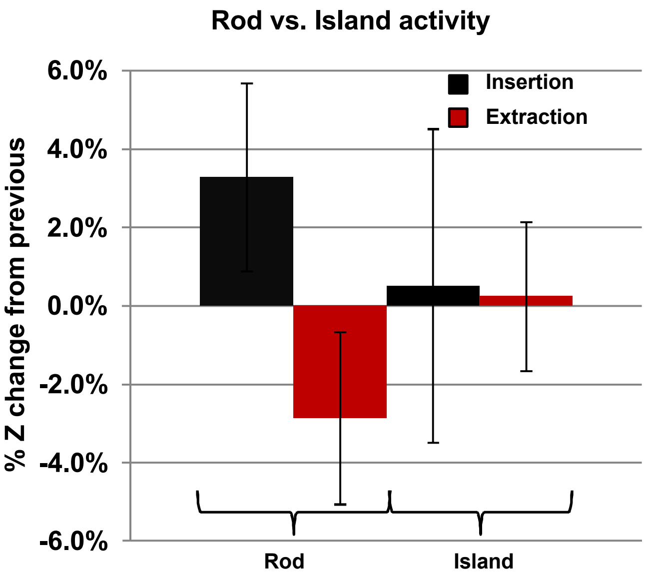
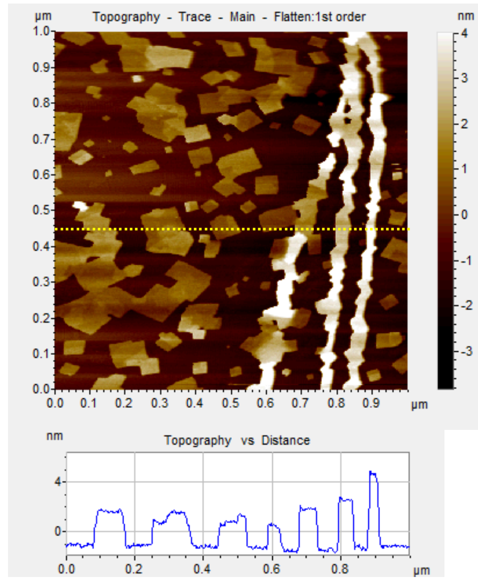
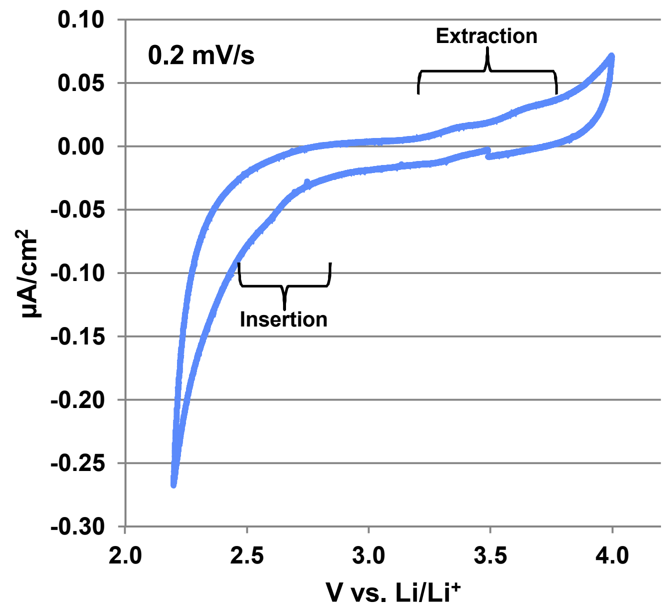
Structure/interface-activity differences

Functionalized graphite





β-MnO_2 voltammetric response is swamped by background - confirms low overall lithiation activity



Total anodic charge would correspond to x = 0.17

Why the activity difference?

- Structural form - ribbons vs. islands
- Z-dimension restriction
- Differences in particle-substrate wiring - step-edge (line defect) vs. terrace (point defect) linkage

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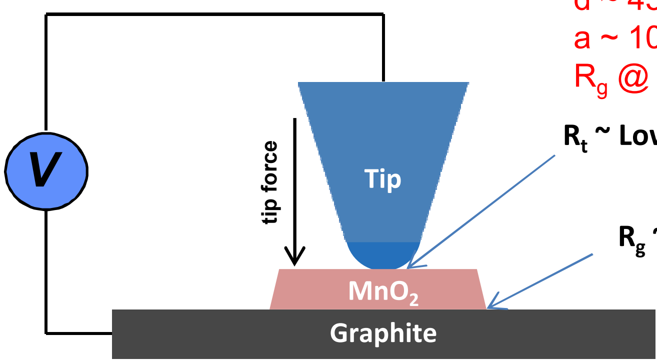
Determining particle-substrate wiring

CAFM:



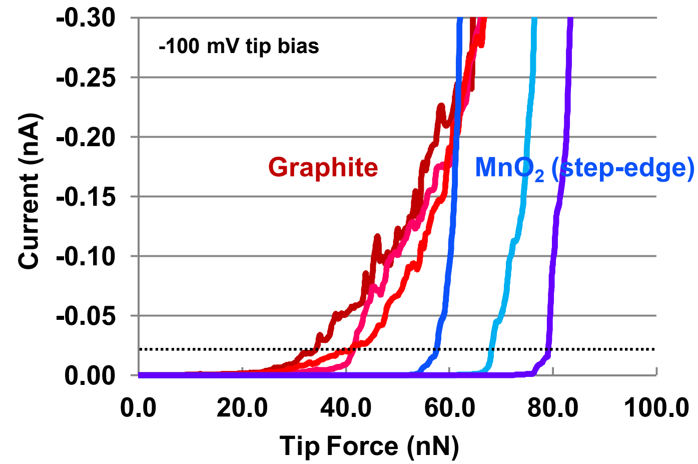
Particle contact area: a = pi*d²/4
d ~ 45 nm
a ~ 10^{-11} cm²
R_g @ 5 Gohm ~ **0.05 ohm*cm²**

R_t ~ Low contact area, low compliance

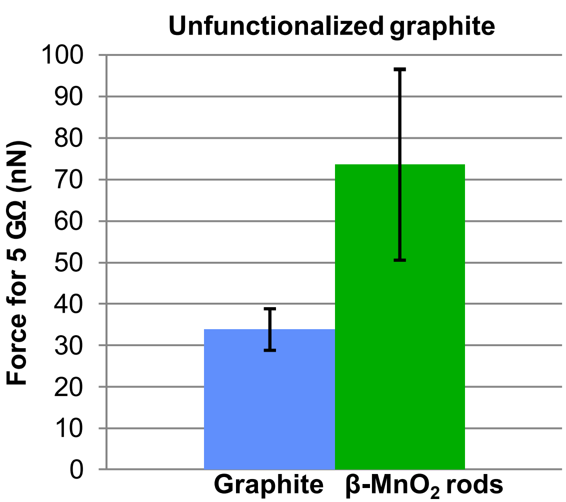
R_g ~ High contact area, high compliance

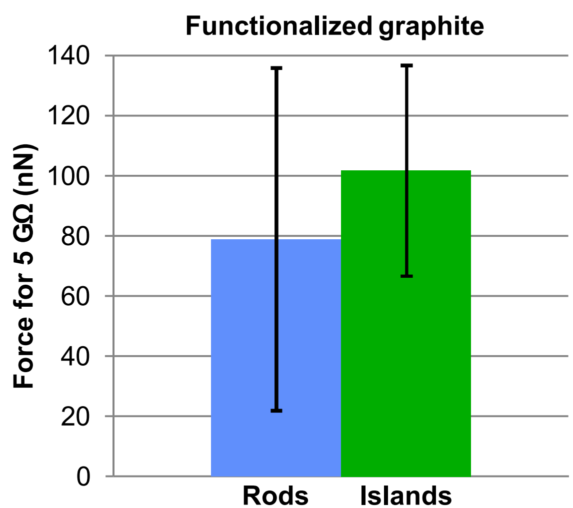
$$R = R_t + R_p + R_g$$

Current-Force spectroscopy convoluted by tip contact mechanics



CAFM wiring statistics from I-F spectroscopy: Ribbons require 70-80 nN, islands require 100 nN.





- **Apparent differences in particle-substrate connectivity: ribbon > island**
  - **Electrical connectivity correlates with apparent adhesion strength**
  - **May explain observed activity differences (in part)**

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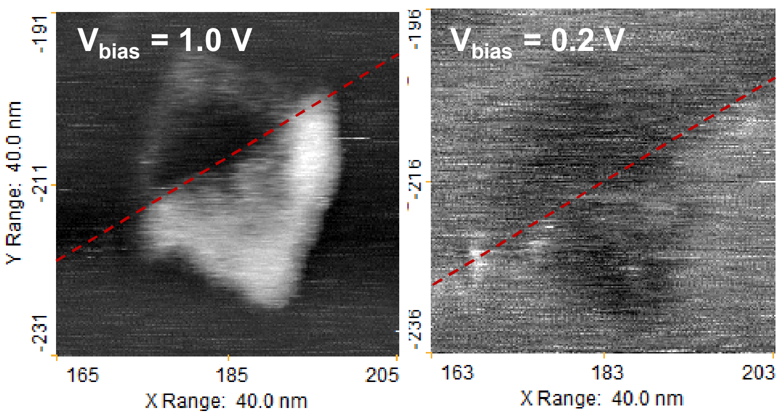
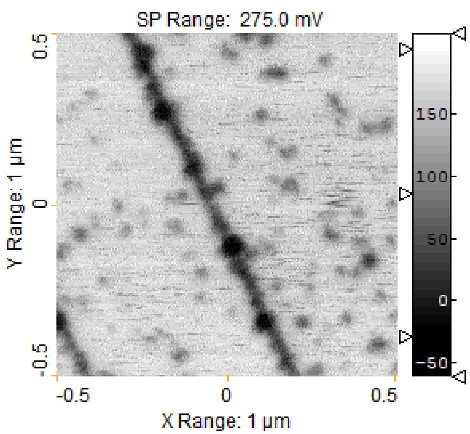
Enabling in situ characterization beyond AFM

SPM electronic property measurements

STM band mapping of $\beta-MnO_2$

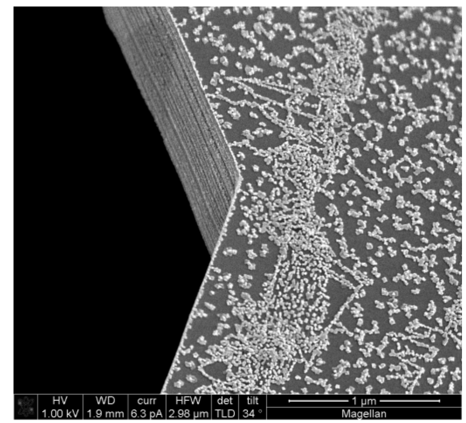


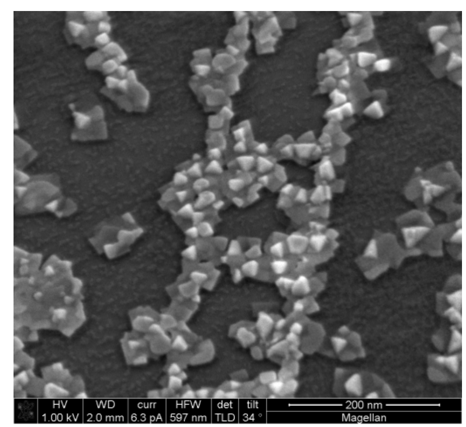
KFM of RuO_2



Goal: measure/map state of charge for either individual structures or populations of structures

Deposition of $LiMn_2O_4$ on graphene TEM grids





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Summary

- **Demonstrated development of a simplified composite electrode system for in situ characterization of metal-oxide nanostructures**
  - ***Exercised control over the formation of β-MnO_2 nanostructures on HOPG through oxygen functionalization***
- **Performed in situ characterization of Li-insertion activity in individual β-MnO_2 nanostructures**
  - ***Demonstrated activity differences between step-edge nanorods and terrace nano-islands, and suggested via CAFM that differences in the MnO_2-C interfacial resistance plays a role***
- **Further application of in situ techniques to the interrogation of these systems is underway**

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Backup Material

Table 1: Formation energy E_d and relative concentrations of common intrinsic defects

Defect Type	E_d, eV	Equilibrium defect concentrations for synthesis at T = 1200 K (CVD)	at T = 3000 K (plasma)
mono-vacancy	7.0 – 7.8	10^{-33}	10^{-13}
di-vacancy	8.7 (HOPG) 4.5 – 5.5 (SWNT)	10^{-38} 10^{-22}	10^{-16} 10^{-9}
interstitial or other covalent sp^3 adduct	5.5	10^{-24}	10^{-10}
Stone Wales 5-7-7-5	3.5	10^{-15}	10^{-6}
single 5-7 defect	3.4 (SWNT)	10^{-15}	10^{-6}

Young's moduli:
Pt ~ 170 GPa
Graphite ~ 36 GPa (out of plane)
MnO_2 ~ ?

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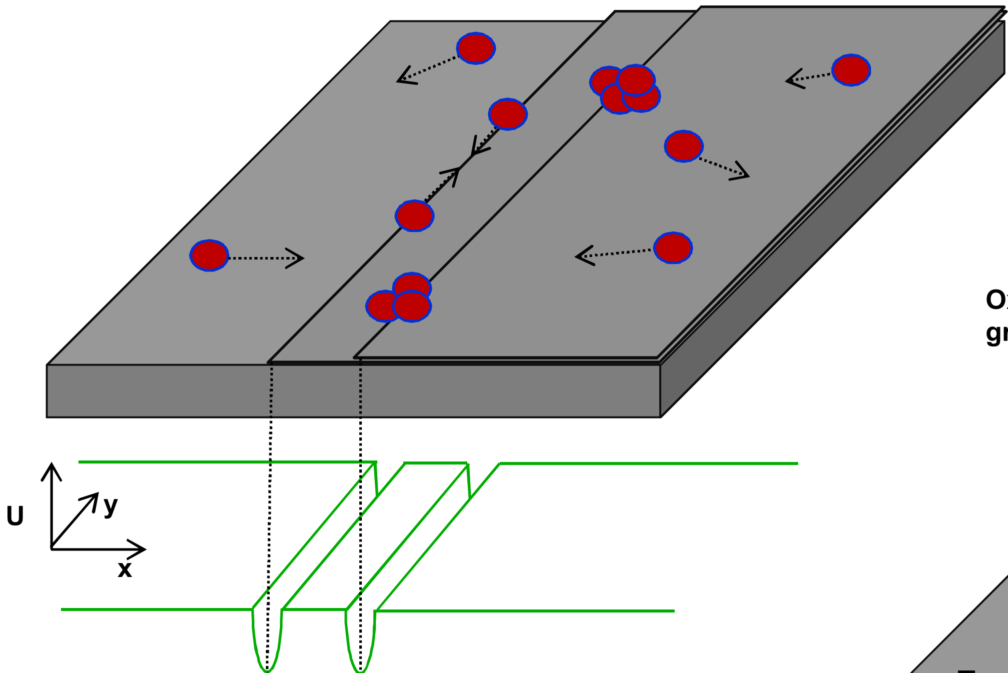
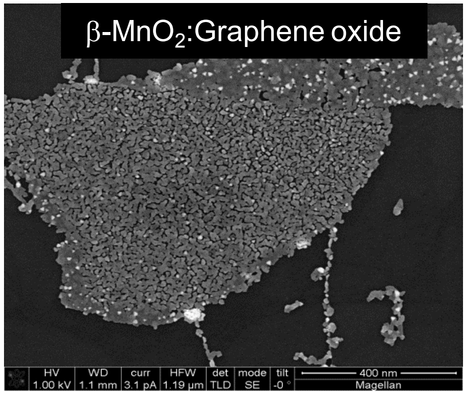
Controlling nucleation and growth of β-MnO_2

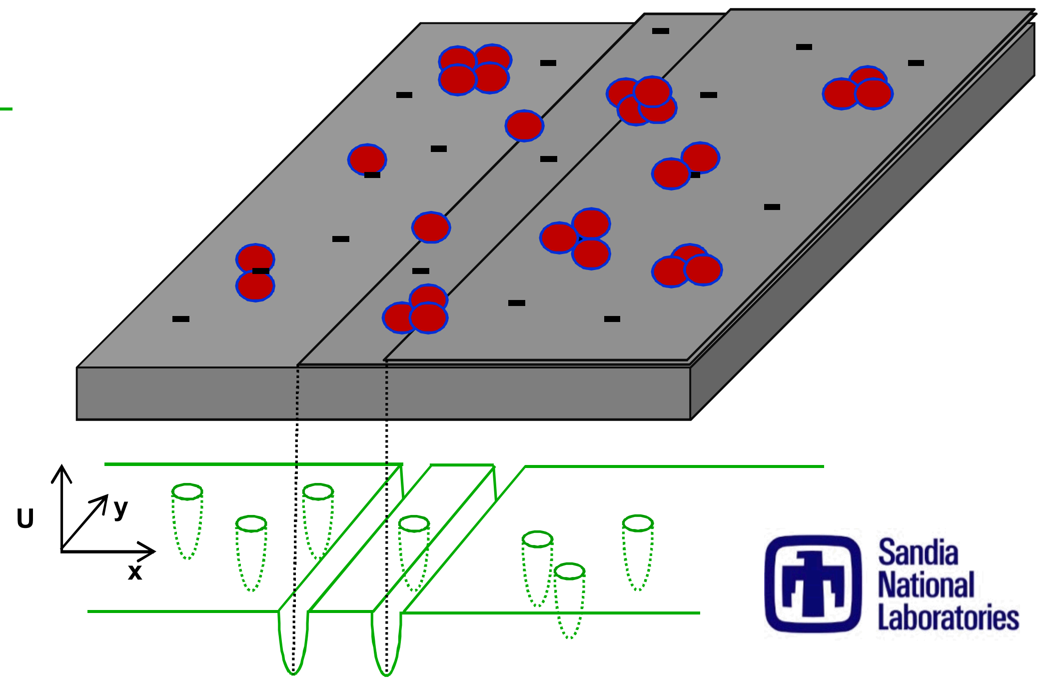
Nucleation/growth model at high temperature: critical cluster size is reached only at step-edges



- **Surface mobility dictated by potential energy landscape**
- **Ad-atoms diffuse rapidly across terraces and along step edges (line defects)**
- **Particle density builds in defect-rich zones until critical cluster sizes are reached (nucleation)**



Oxygen functionalization presents many nucleation sites on graphite terraces



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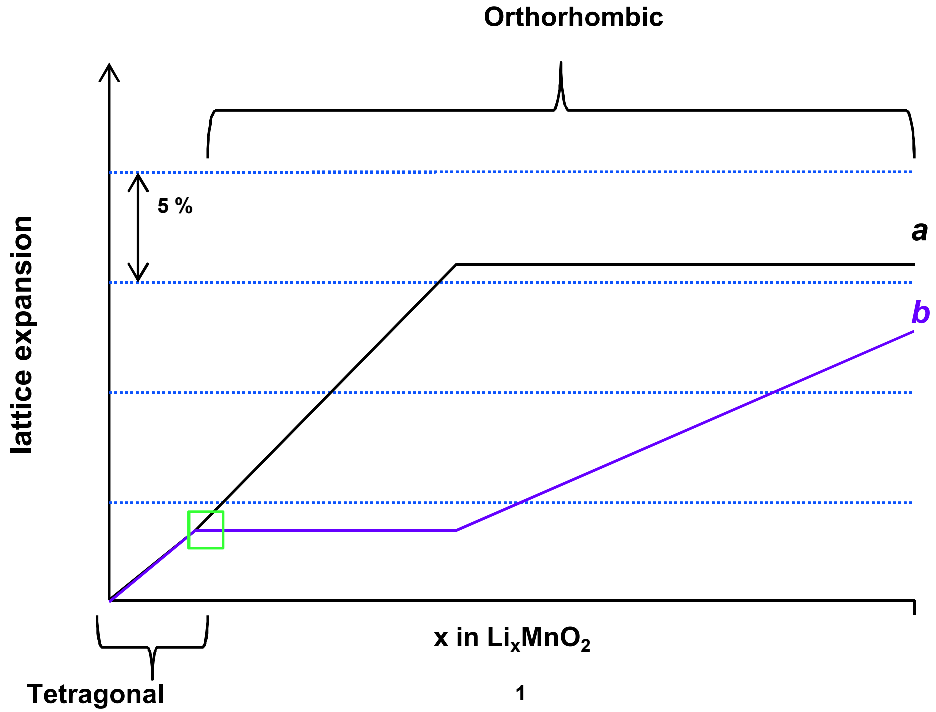
Why only 3-4%?



Orthorhombic
5 %
a
b
lattice expansion
x in Li_xMnO_2
Tetragonal
1

Comments

- Acknowledgements to background info collaborators
- Indicate/discuss dimensional changes of nanoribbon - line scans illustrating growth
- Further placement of height change measurements in context of literature
- Include voltammetry data as evidence of low particle activity
- See if particle activity depends on height
- Further study of 13% height change case
- Study TEM lattice parameters to look for consistencies in lattice parameter across particle height