Phase Evolution and Interfaces in Electrode Materials for Energy Storage

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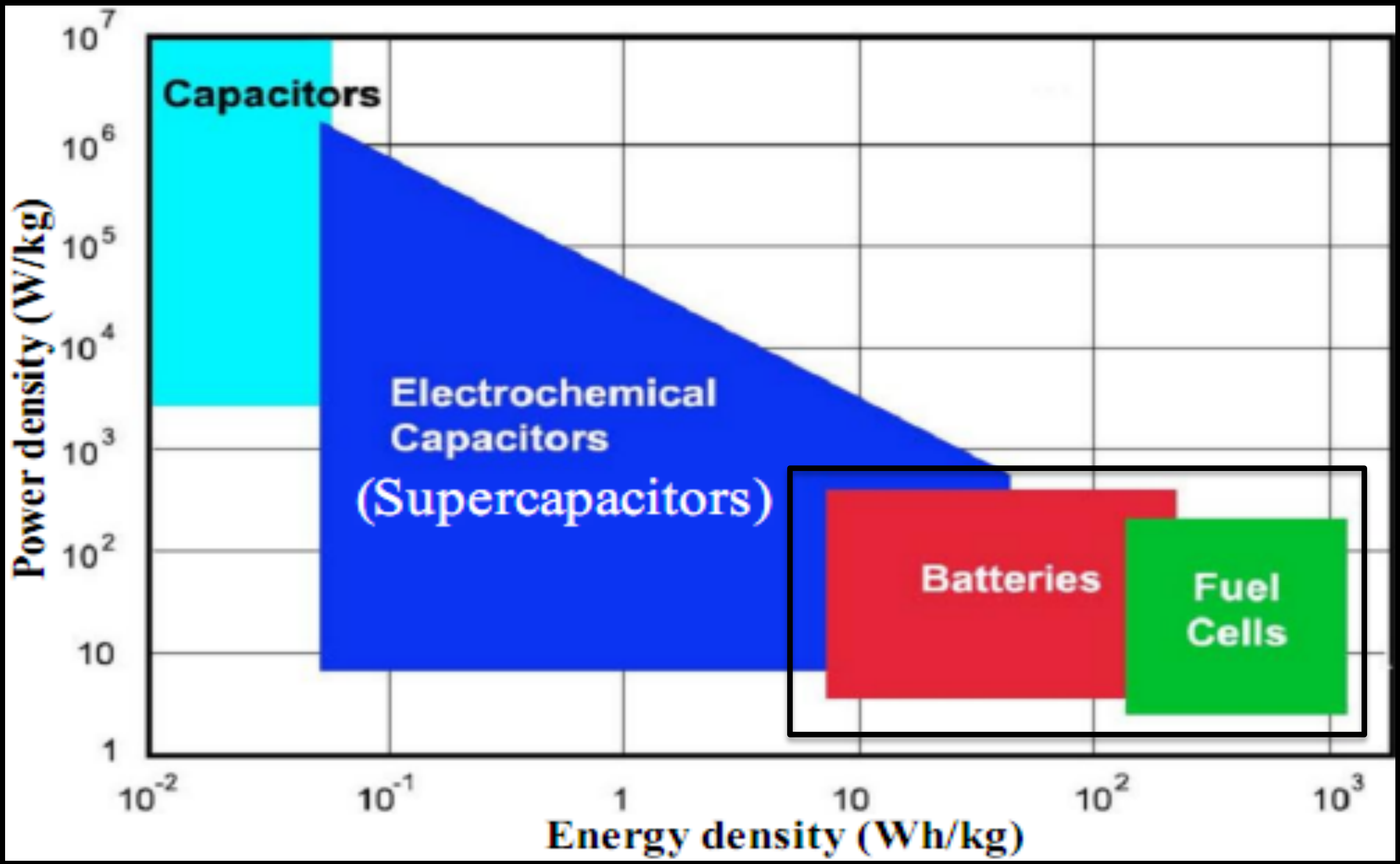
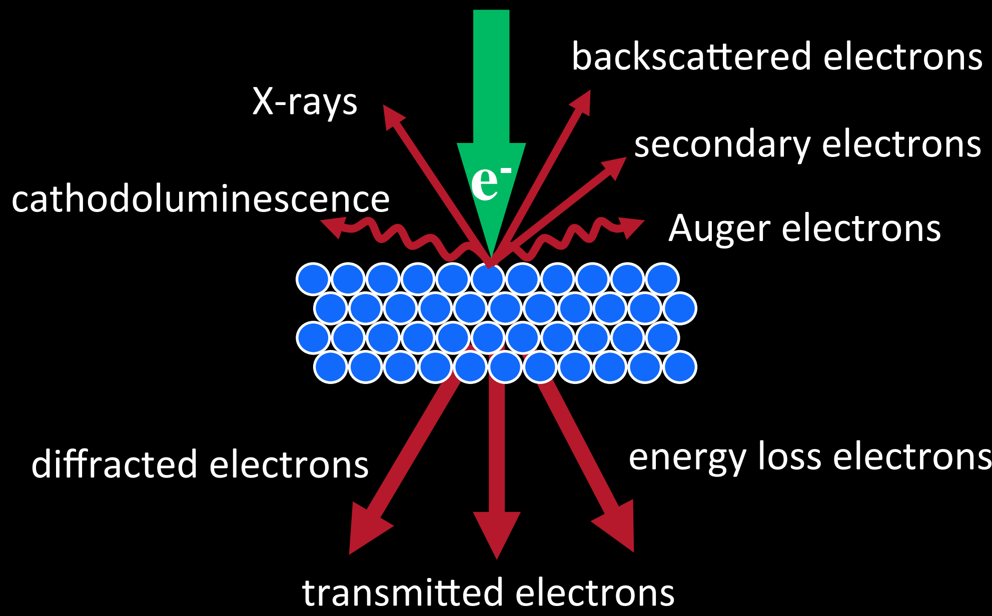
Energy Storage: Fuel Cell vs Batteries

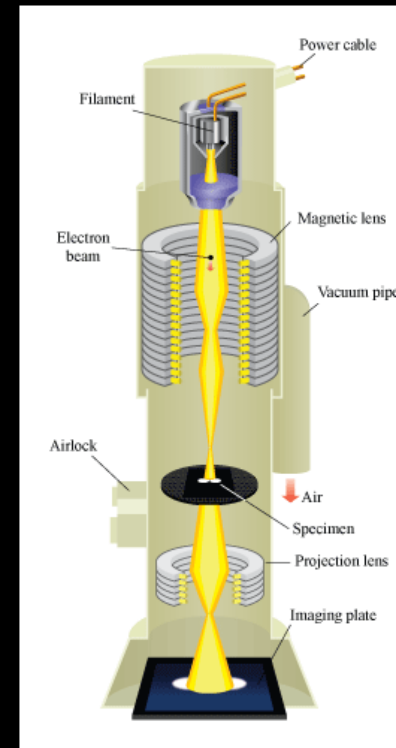


Outline

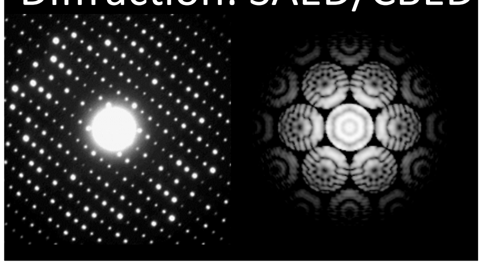
- Introduction:
  Advanced Transmission Electron Microscopy
- Structure-Property relation of Electrode Materials
  (i) Fe_3O_4 nanoparticle and thin film for LIB
  (ii) PtPb-Pt nanoplate catalyst for fuel cell
- Outlook

TEM: Transmission Electron Microscopy(e)

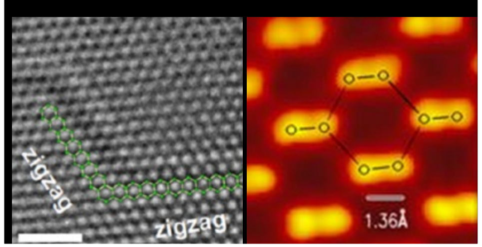




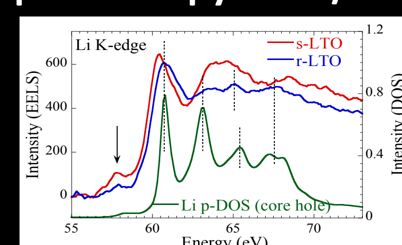
Diffraction: SAED/CBED



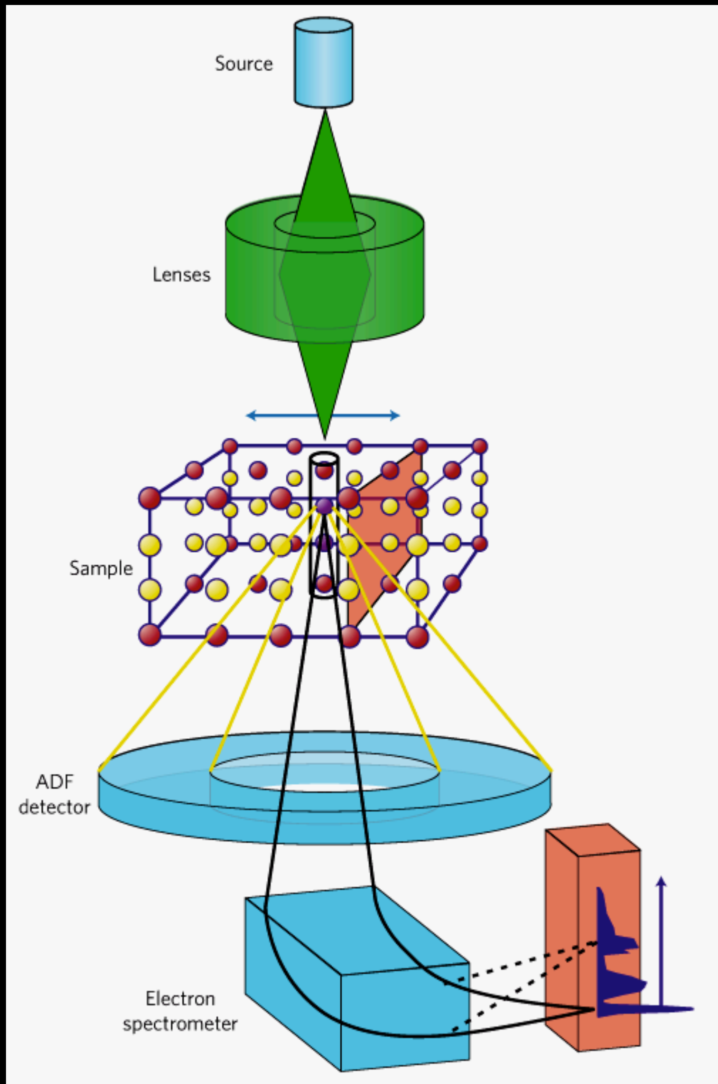
Imaging: TEM/STEM



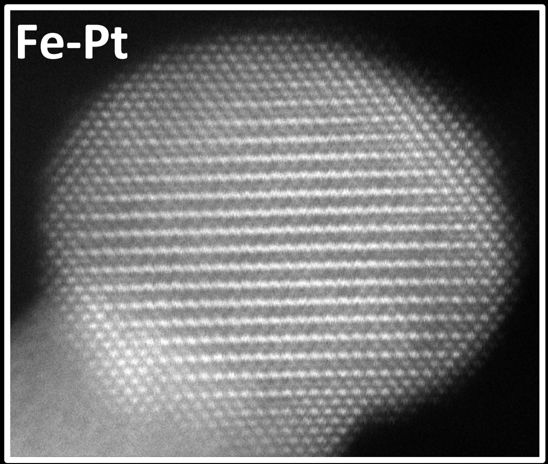
Spectroscopy: EELS/EDX



STEM : Scanning Transmission Electron Microscopy

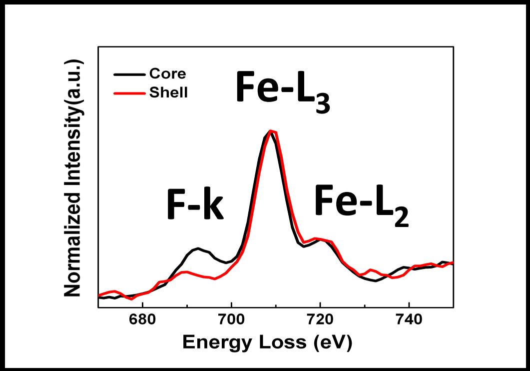


High-angle annular dark field (HAADF)



Li, Su, Sun et al. Nano Letters, 2015

Electron energy-loss spectroscopy (EELS)

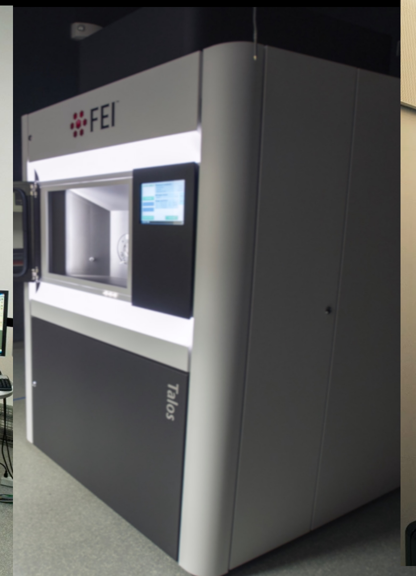


Kim, Su, Wang, et al. ACS Nano, 2015

Transmission Electron Microscopes at CFN

JEOL 1400

JEOL 2100F



FEI-Talos 200

Hitachi HD2700C

Titan 80-300 - ETEM

Capability:

Versatile
analytical & in-situ TEM

Analytical STEM
STEM-EELS

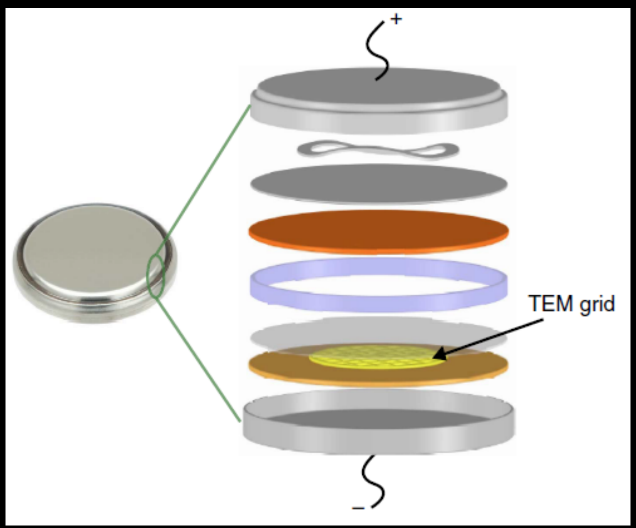
Soft & biological
materials

Analytical instrument:
3D STEM and STEM-EDX

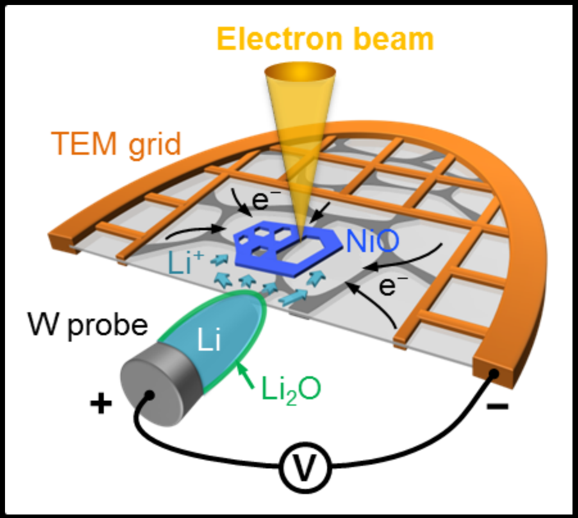
Environmental &
in-situ TEM

Approach: Combine Ex-situ and In-situ TEM

ex situ TEM
(port-mortem)



in situ TEM
(dry cell)



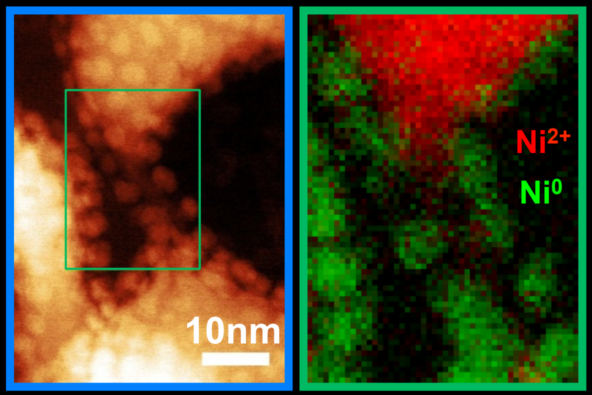
X-ray
(ensemble-average)

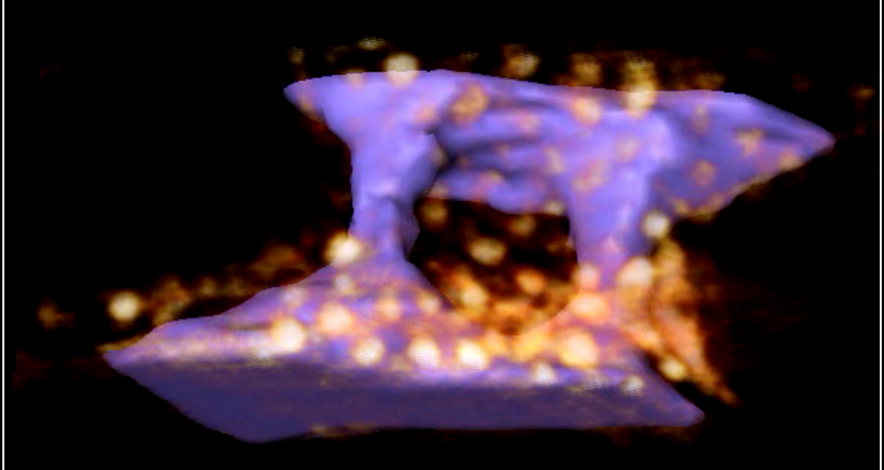
Correlating TEM results with other measurements

Huang et al. Science 330,1515 (2010)
Lin *et al*. Nature Comm. 5, 3358 (2014).
He, Su *et al*. Nano Lett. 15, 1437 (2015).

Example : Reaction interface of Sodiation of NiO

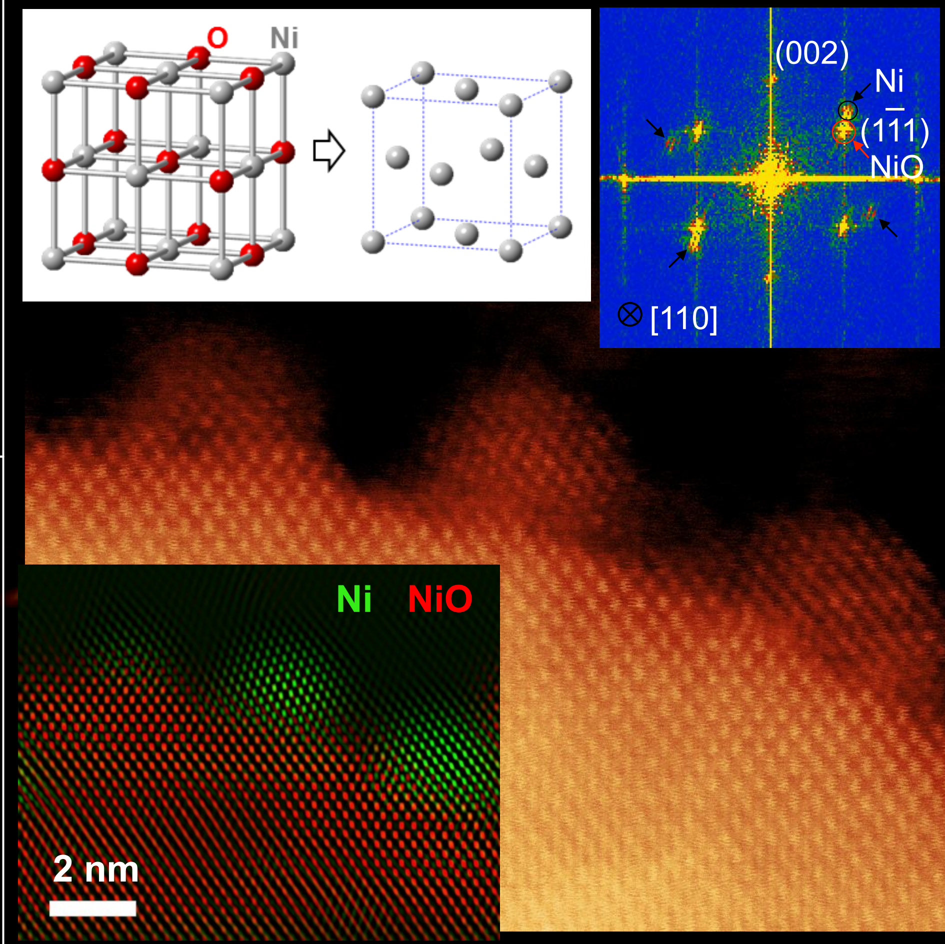
Valence-state mapping using STEM-EELS





3D tomography

Atomic-resolution ADF-STEM

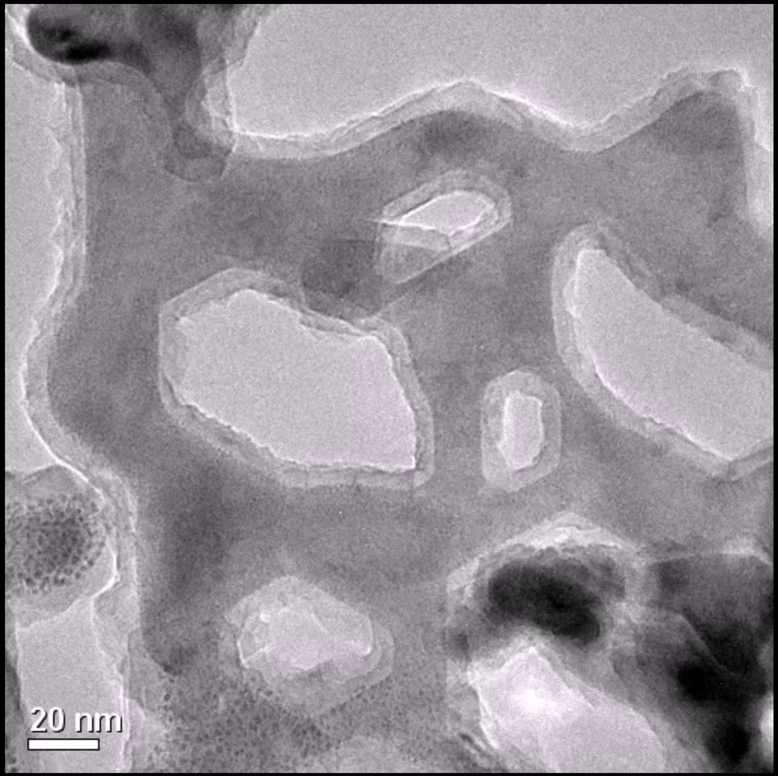


$$NiO + Na^{+} + e^{-} \rightarrow Na_2O + Ni$$

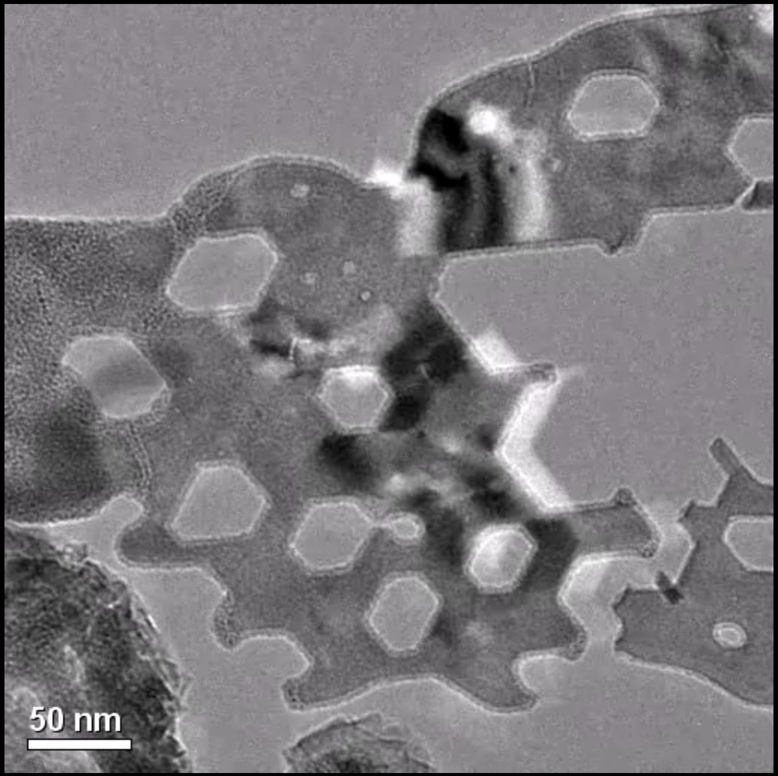
He, *et al.* and Su, Nano Lett. 15, 5755 (2015).

Example: In-situ TEM of Sodiation vs Lithiation

Sodiation



Lithiation



$NiO + Li^{+}/Na^{+} + e^{-} \rightarrow Li_2O/Na_2O + Ni$

Same reaction different reaction process!

He, *et al.* and Su, Nano Lett. 15, 5755 (2015).

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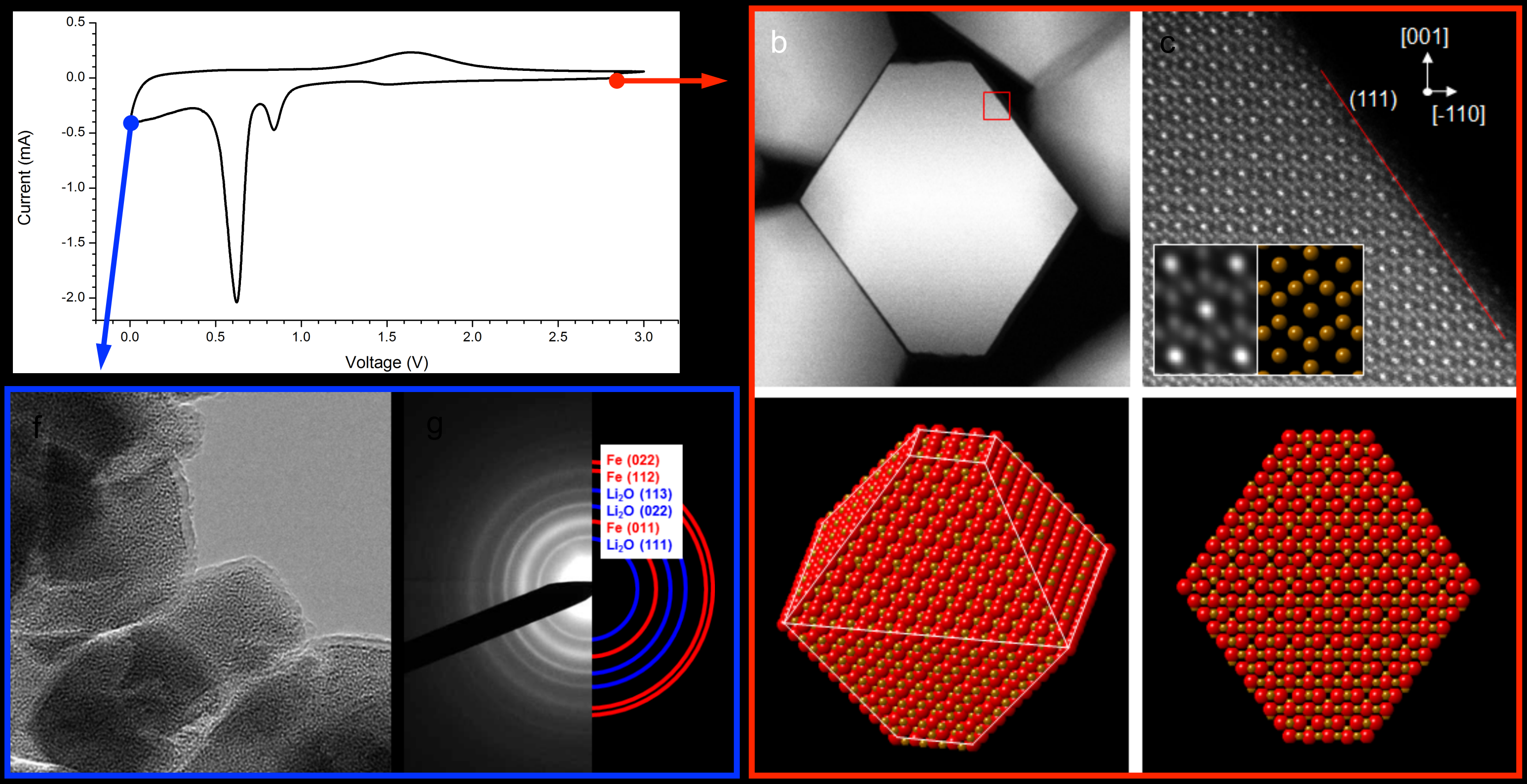
Lithiation of Inverse Spinel Fe_3O_4

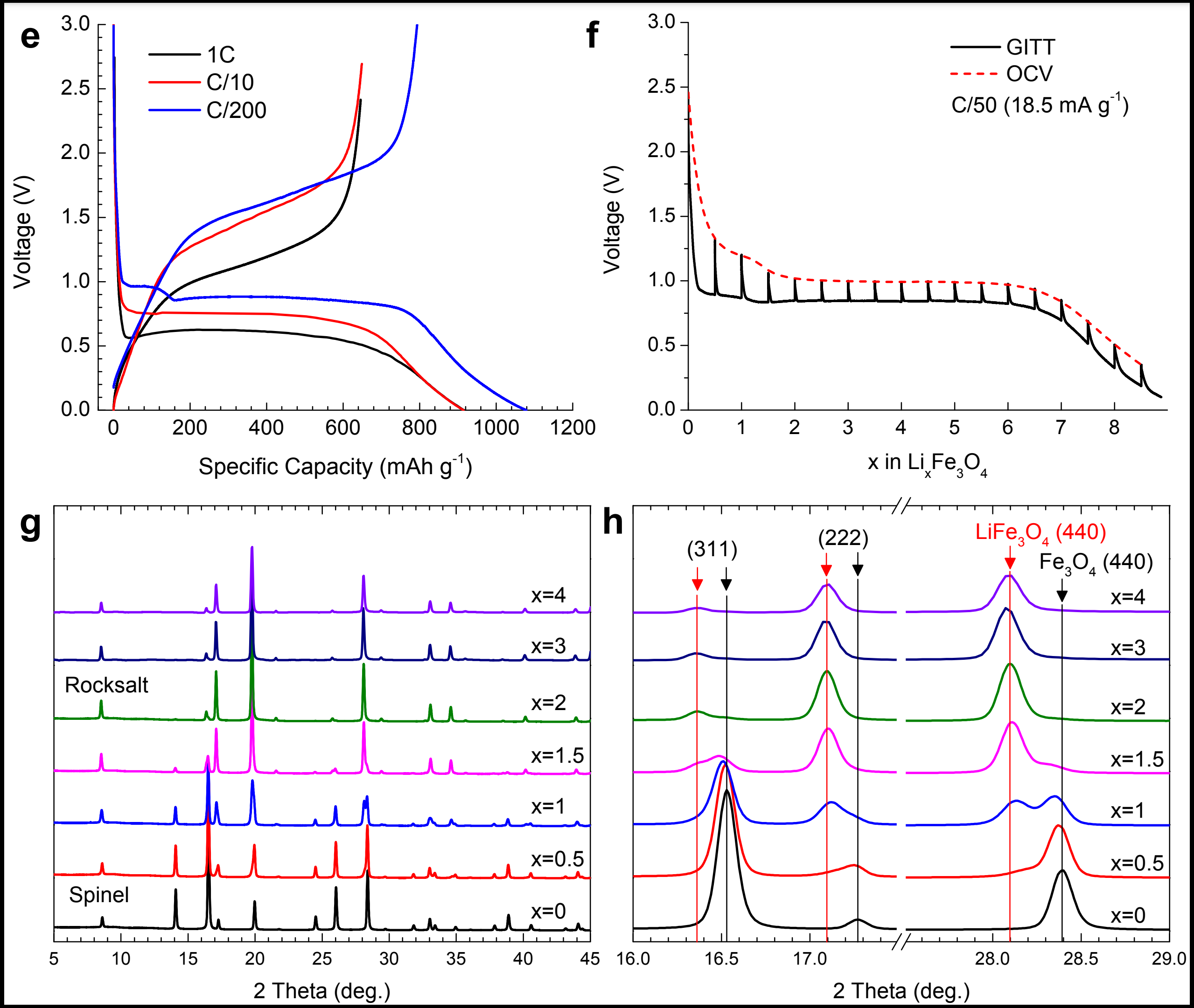


$8\ Li^{+} + 8\ e^{-} + Fe_3O_4 \rightarrow 4Li_2O + 3Fe$

Capacity: 926 mAh/g

Samples from Chris Murray at Penn

Lithiation of Fe_3O_4: Intermediate Phase



Fe_3O_4

↓

$LixFe_3O_4$

↓

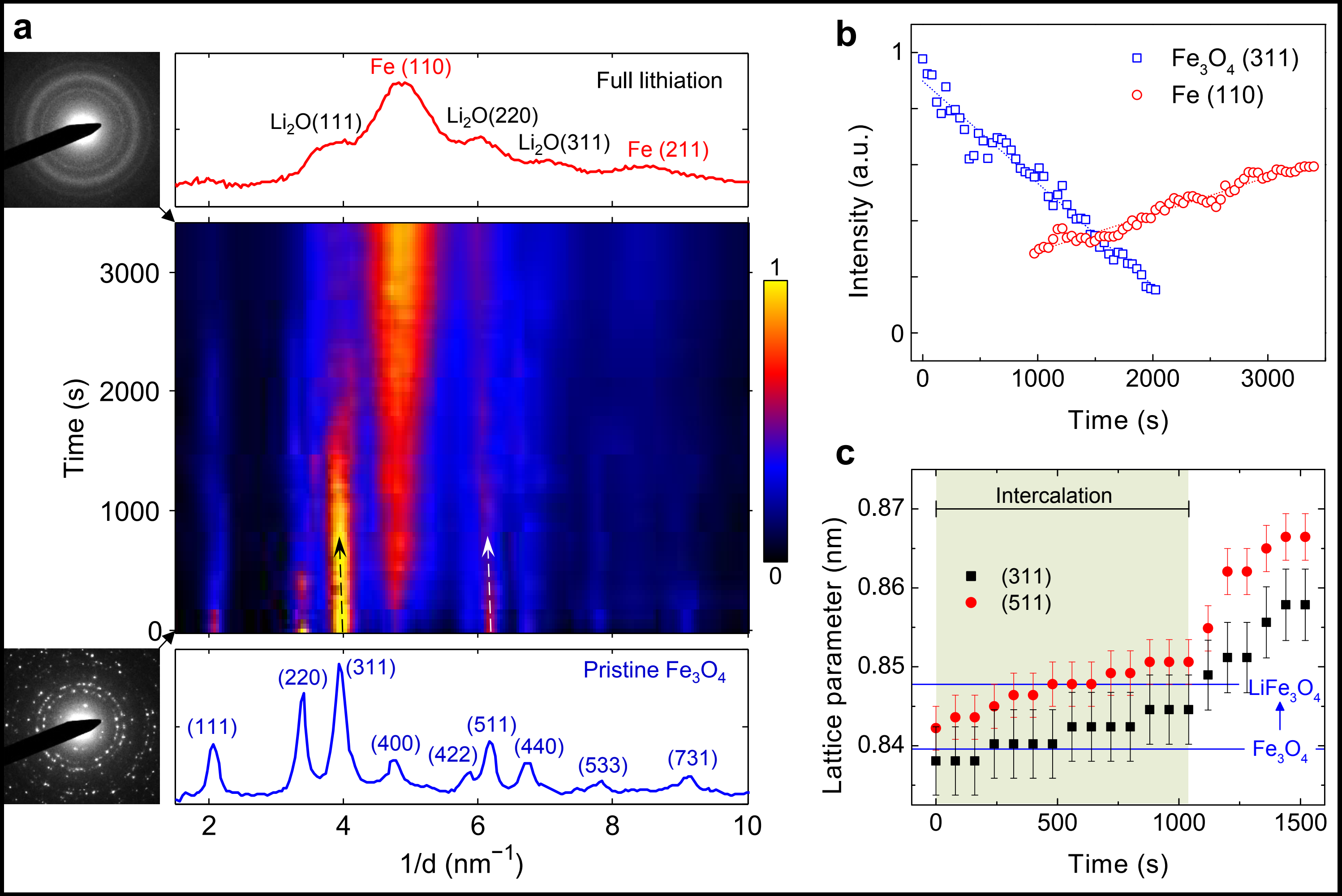
???

↓

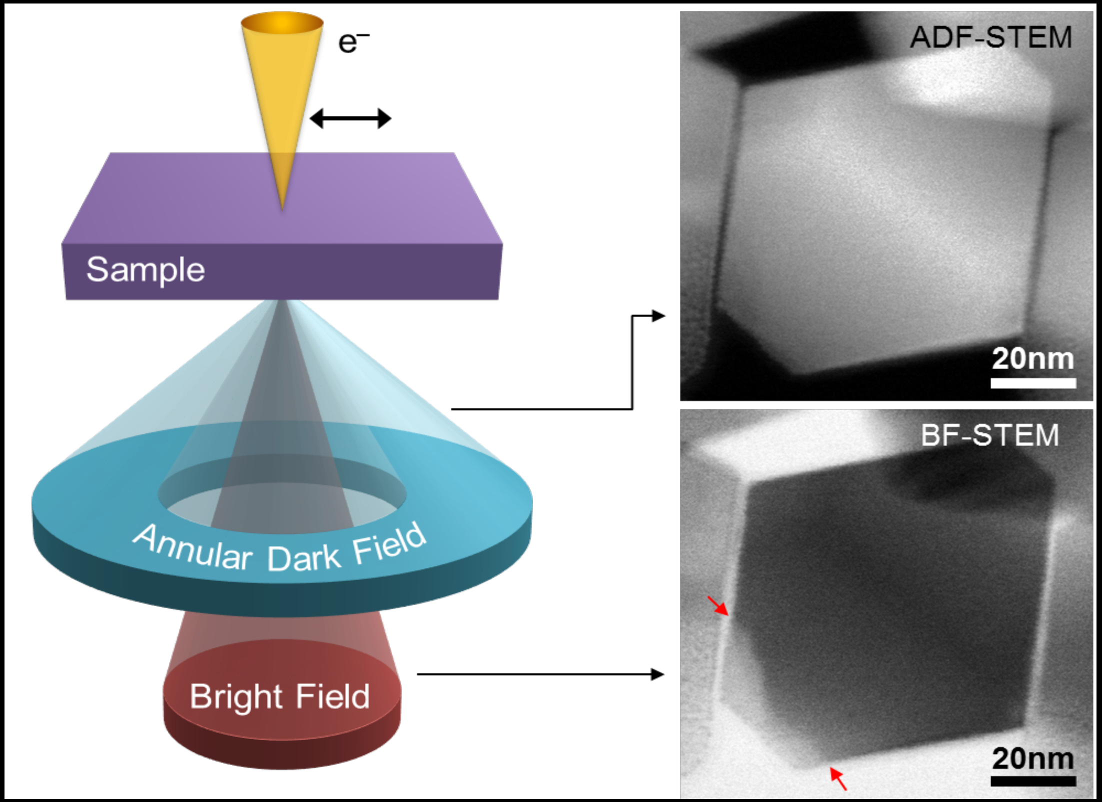
Li_2O +Fe

He, *et al.* Murray and Su, Nature Comm. 7, 11441 (2016)

In-situ Electron Diffraction

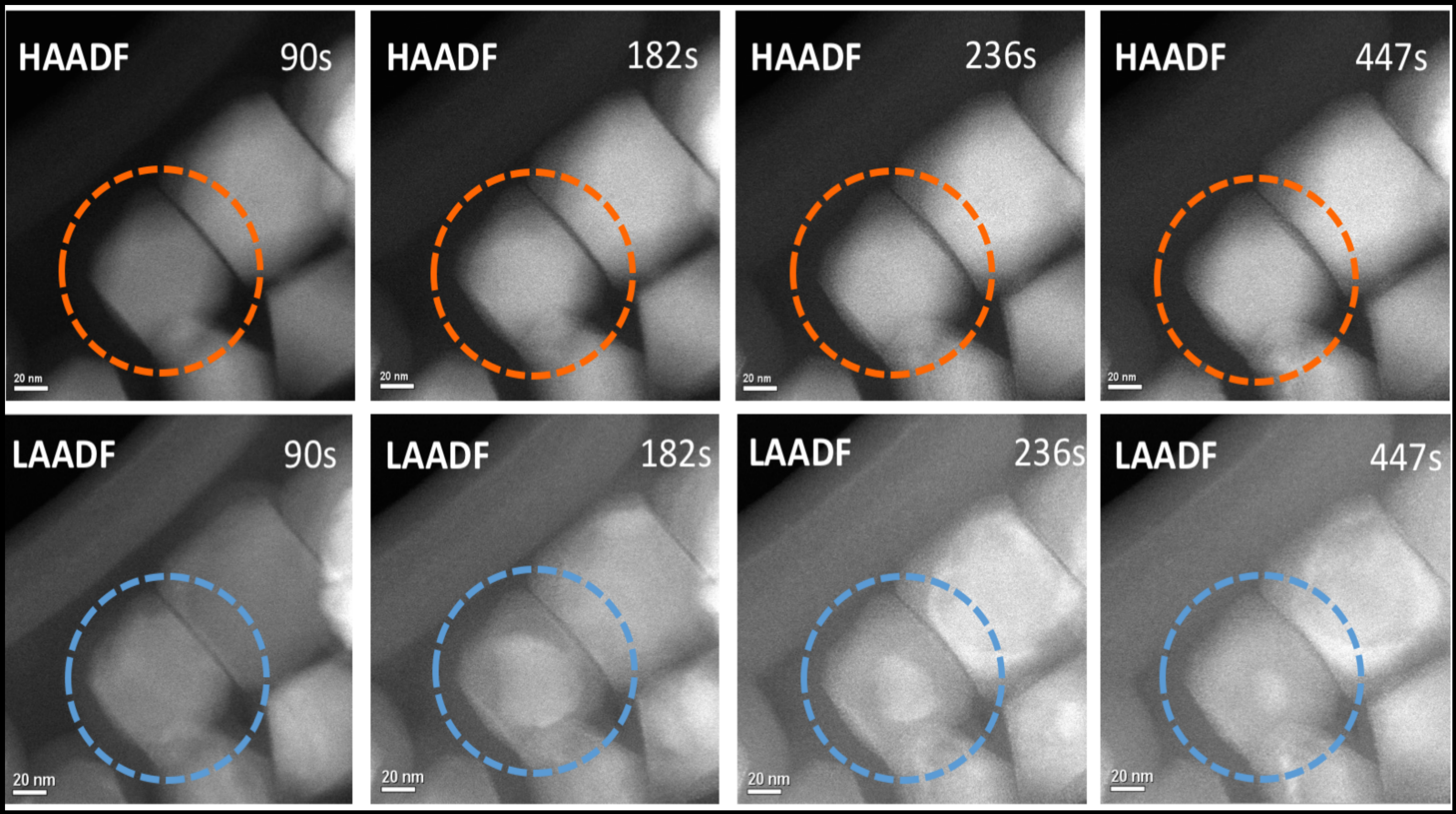


Strain Sensitive STEM Imaging: BF/LAADF



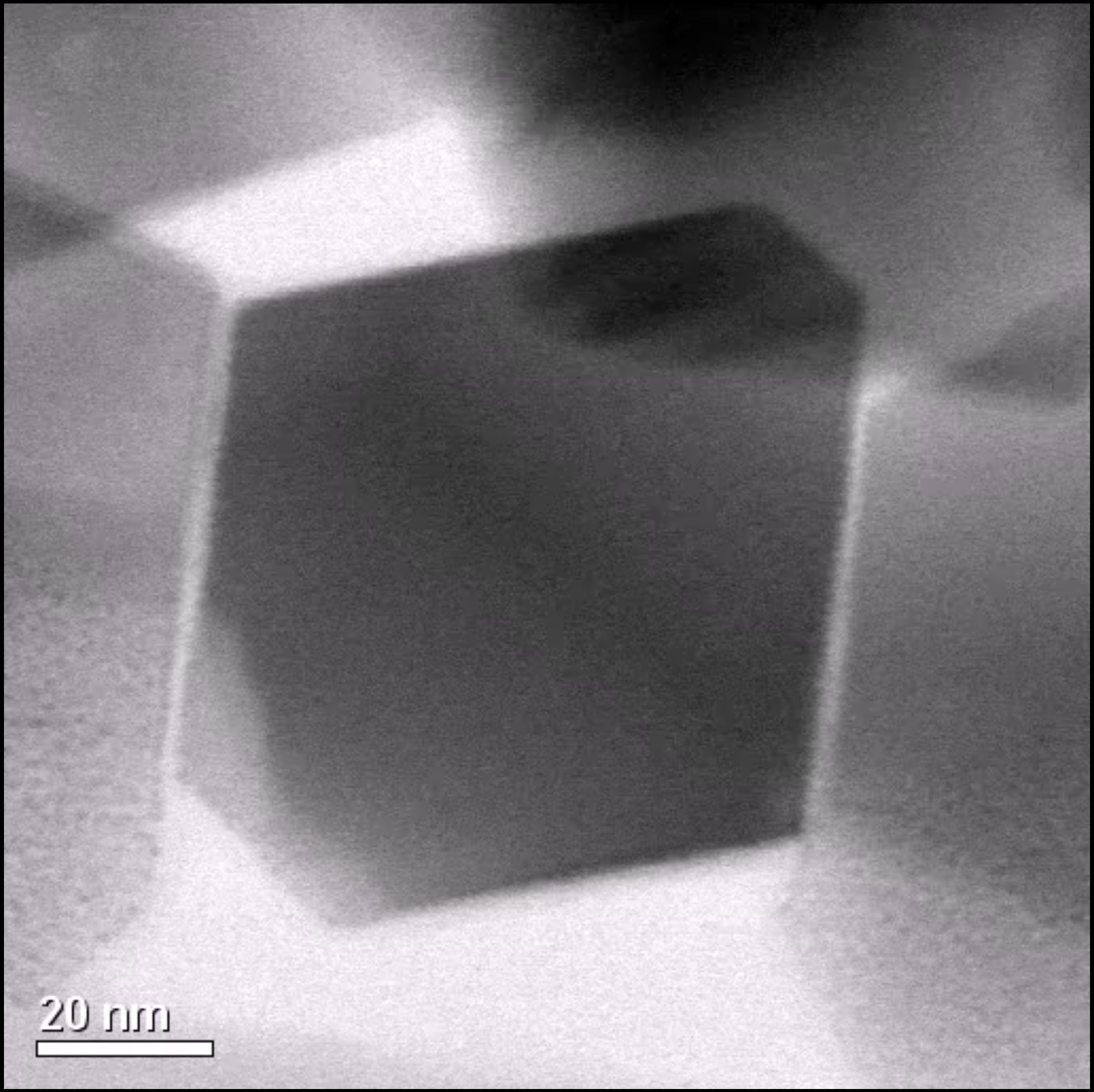
Strain-sensitive: Bright-Field mode or Low-angle ADF mode

Comparison Between HAADF and LAADF



Li, et al. and Su, ACS Nano, 10, 9577(2016)

In-situ Bright-Field STEM

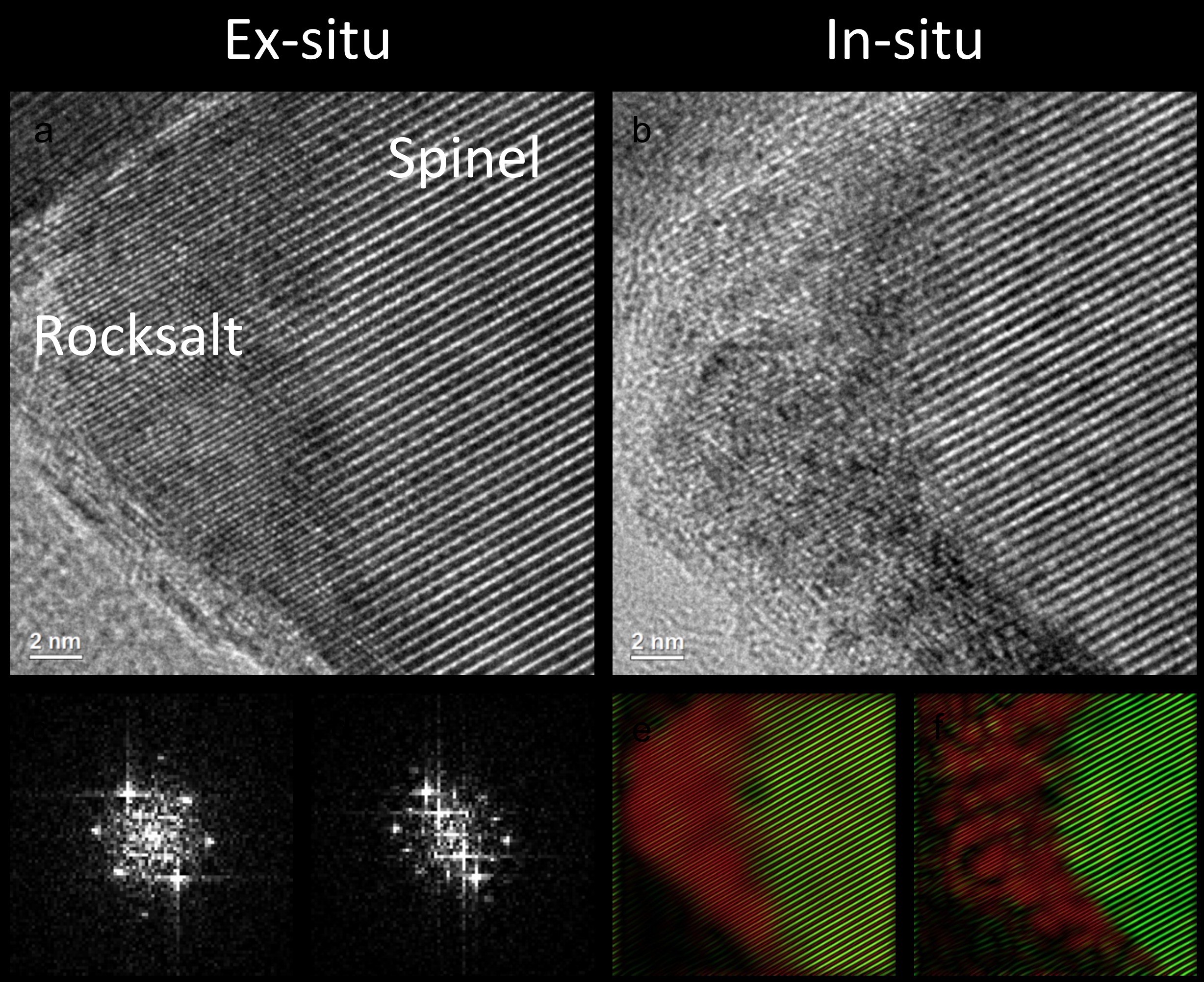


Fe_3O_4

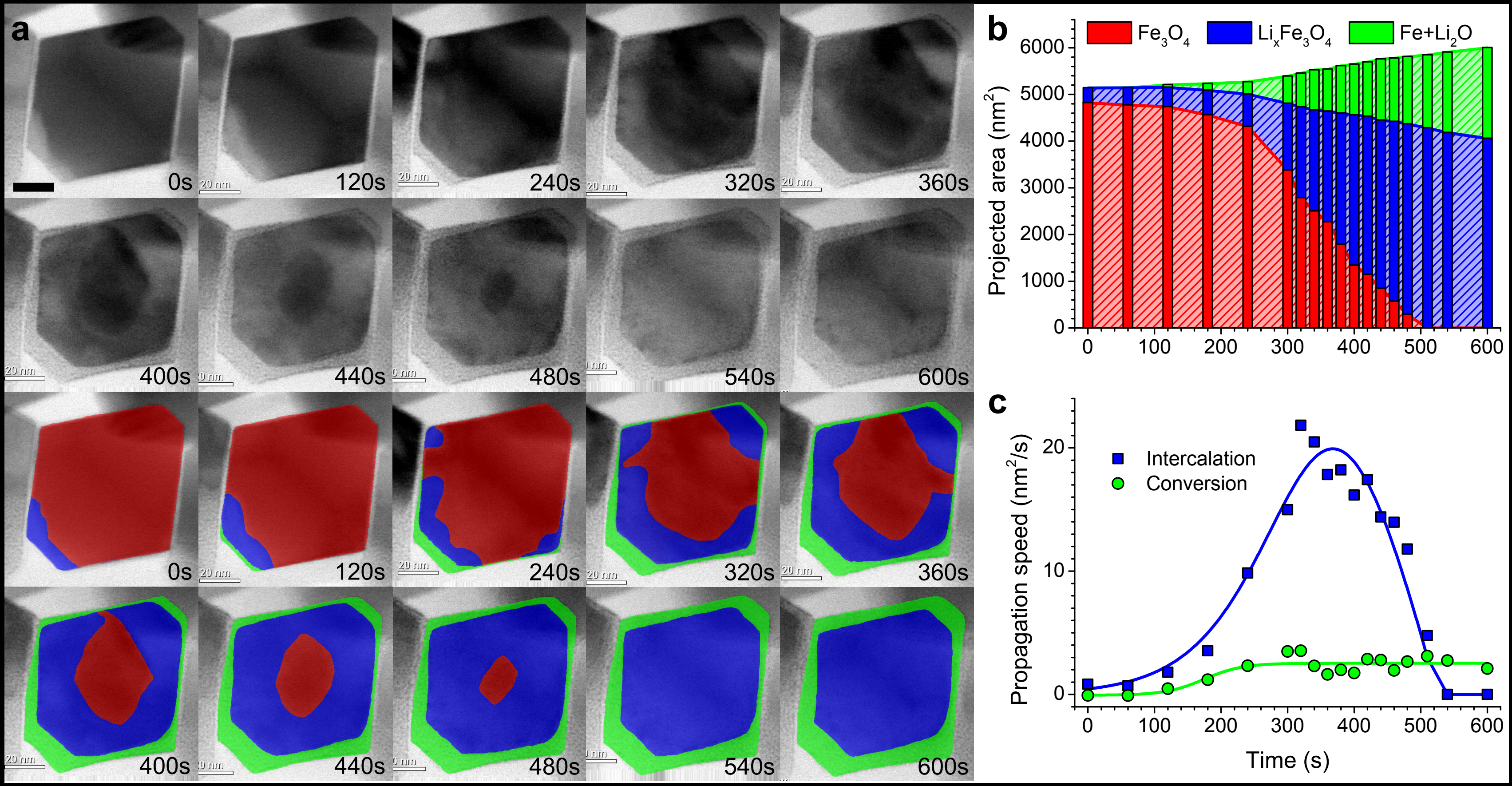
$LiFe_3O_4$

Li_2O +Fe

HR TEM of Ex-situ/In-situ Samples



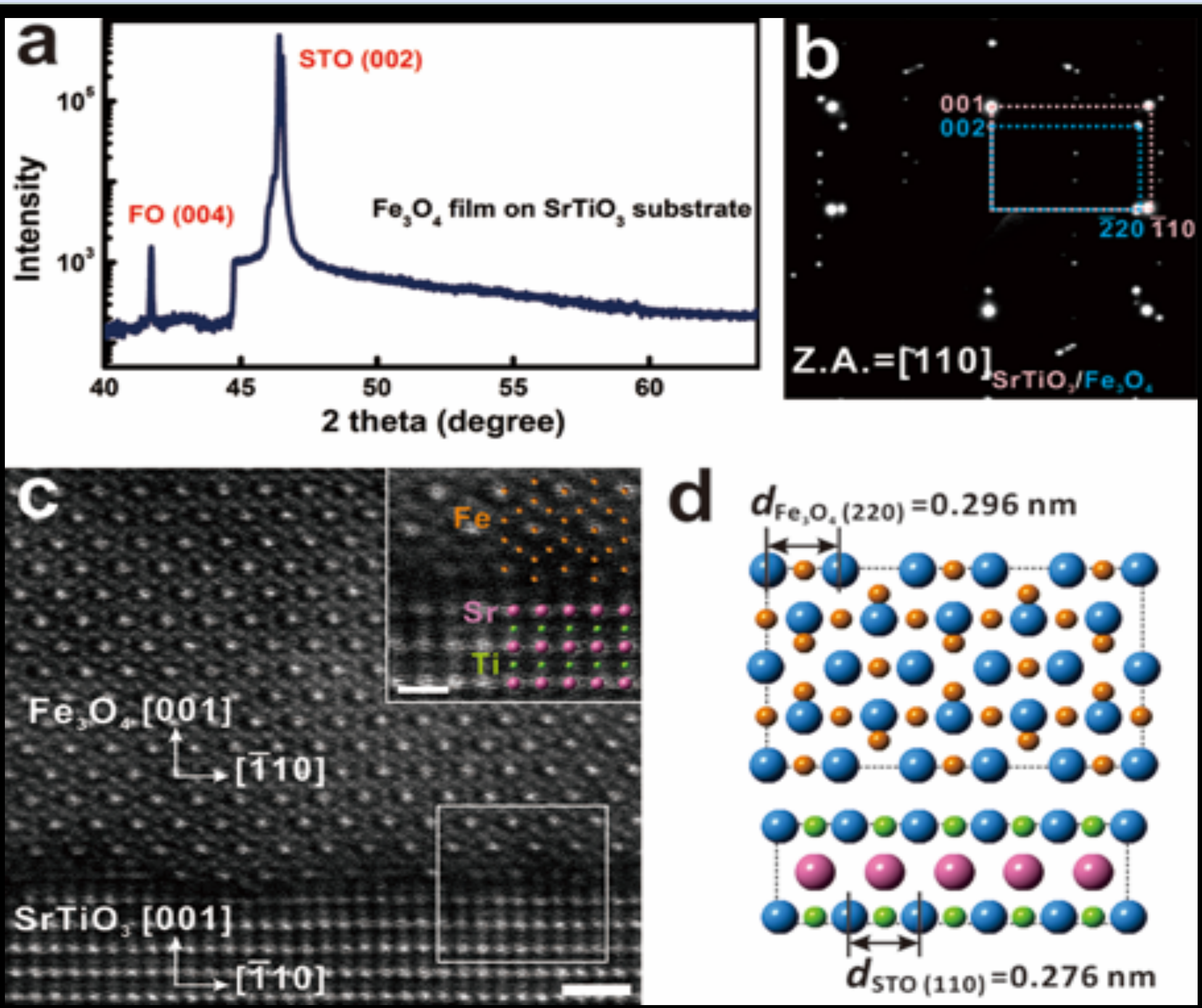
In-situ BF-STEM: Reaction Inhomogeneity



- The lithiation of nanomaterial is highly inhomogeneous

He, *et al.* Murray and Su, Nature Comm. 7, 11441 (2016)

Fe_3O_4 Epitaxial Thin Film

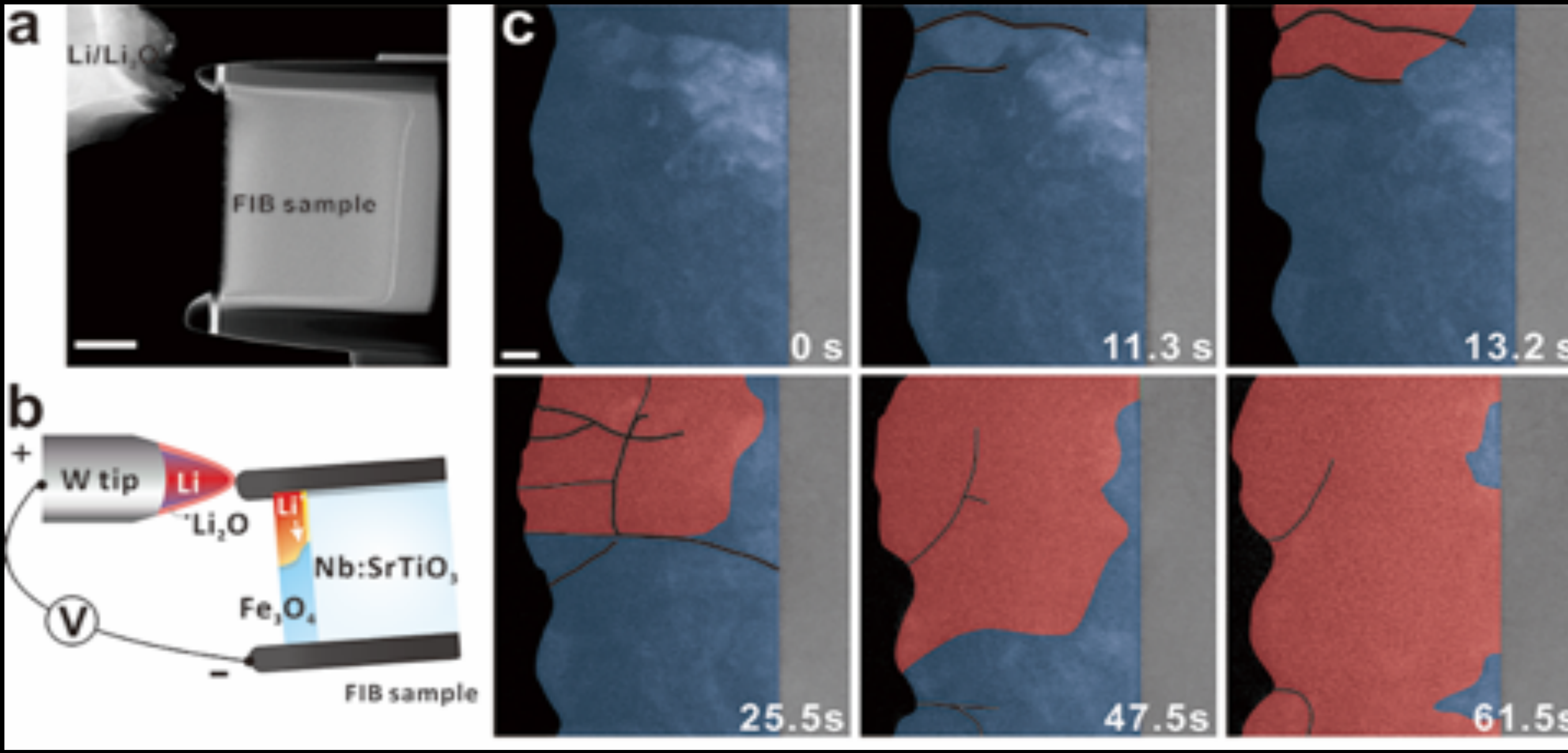


Under compressive strain from substrate, partially relaxed by interfacial defects

Samples from Ying-Hao Chu's group

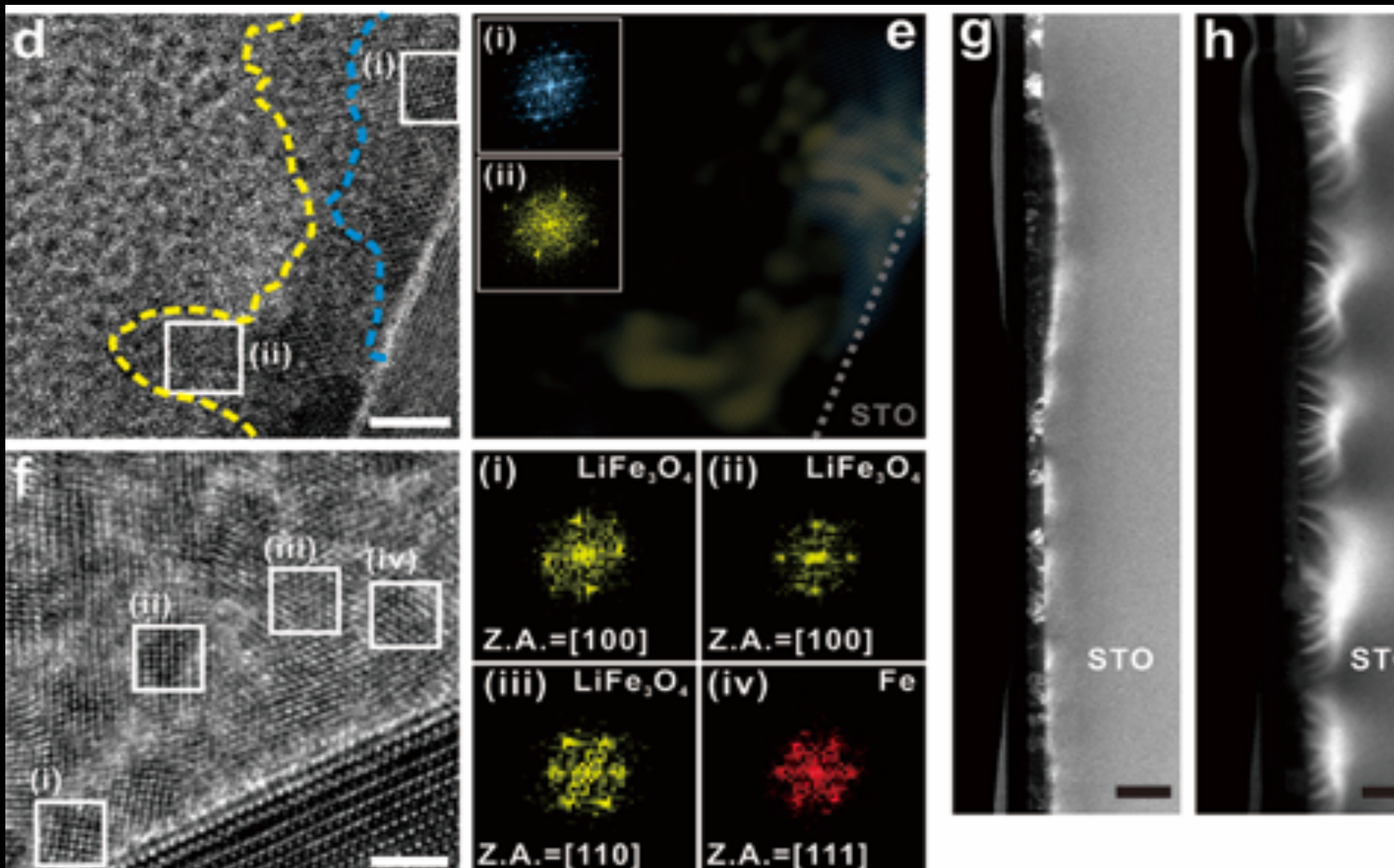
Hwang, *et al.* and Su, Angewandte Chemie, (2017)

In-situ STEM on Lithiation of Fe_3O_4 Film



- Formation of cracks at upper film
- Non-conversion area close to Fe_3O_4/$SrTiO_3$ interface

Phase Identification



- The formation of rock-salt phase close to interface

Phase Field Simulations: Formula

Lithium diffusion inside Fe_3O_4 : Cahn-Hilliard equation

$$\frac{\partial c}{\partial t} = \nabla M c \nabla(\Delta\mu)$$

Strain field in Fe_3O_4 thin film described by van Der Merwe's t heory:

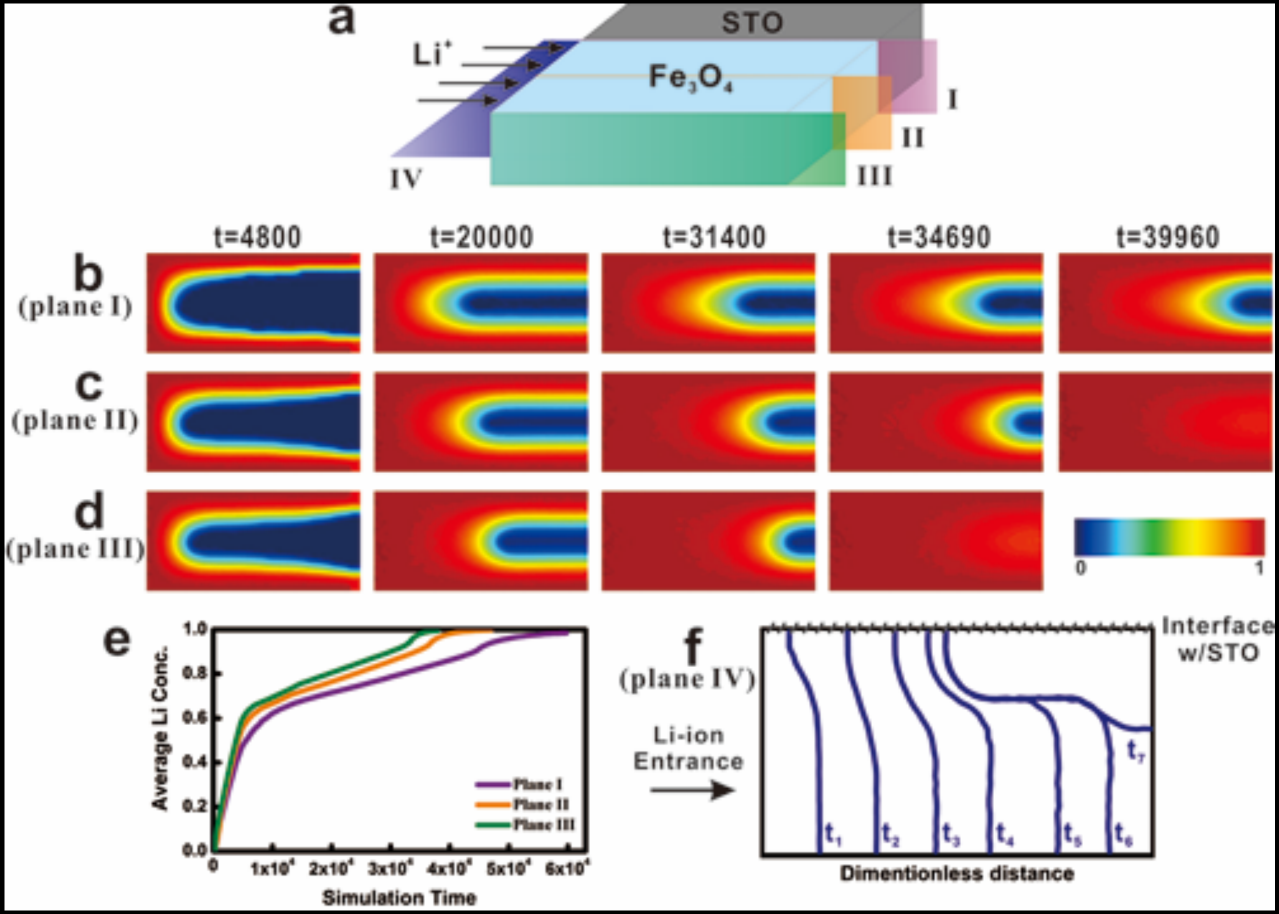
$$\varepsilon_{ii}^{(in)} = \varepsilon_0^{(in)} \exp(-ax)$$

Strain coupling:

$$f_{el\_c} = \frac{1}{2} K \varepsilon_{ii}^{(in)} \varepsilon_{ii}^{(0)}$$

J. Newman, *Electrochemical Systems*, Prentice Hall, **1991**.
J. H. Van der Merwe, *Proc. Phys. Soc. 63*, 616–637,(1950)
M. Tang, *et al.* and Y.-M. Chiang, *Chem. Mater. 21*, 1557–1571, (2009)

Phase Field Simulations: Surface vs. Bulk



Hwang, et al. and Su, *Angewandte Chemie*, DOI: 10.1002/ange.201703168, (2017)

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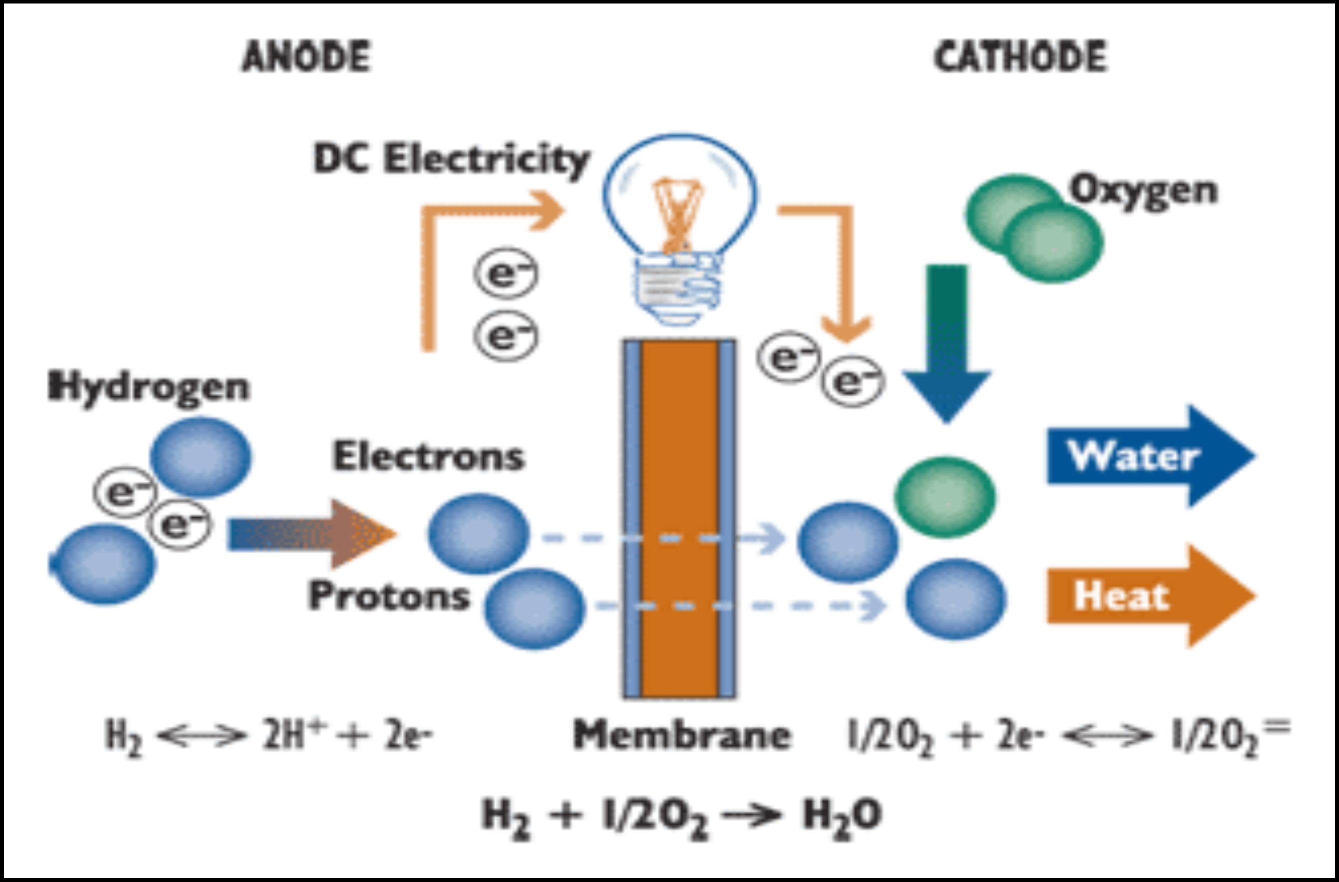
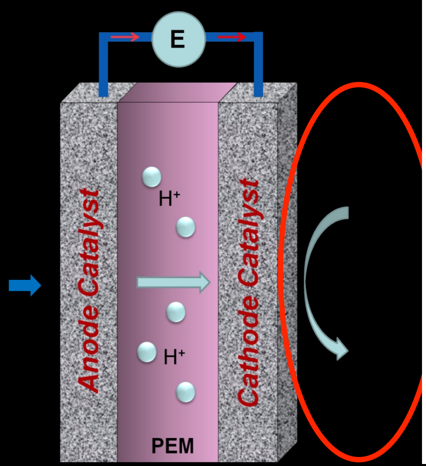
PEMFC： Proton-exchange membrane fuel cell

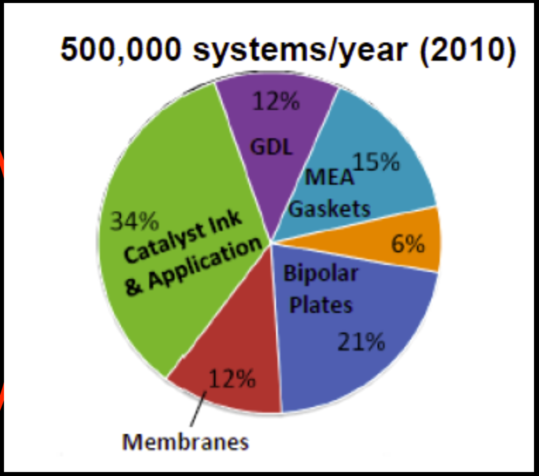


ORR: $O_2 + 4H^+ \rightarrow 2H_2O$

Fuel Cell: Target vs Reality

❑ **Fuel Cell Device**





State of the art of Pt nanoparticle

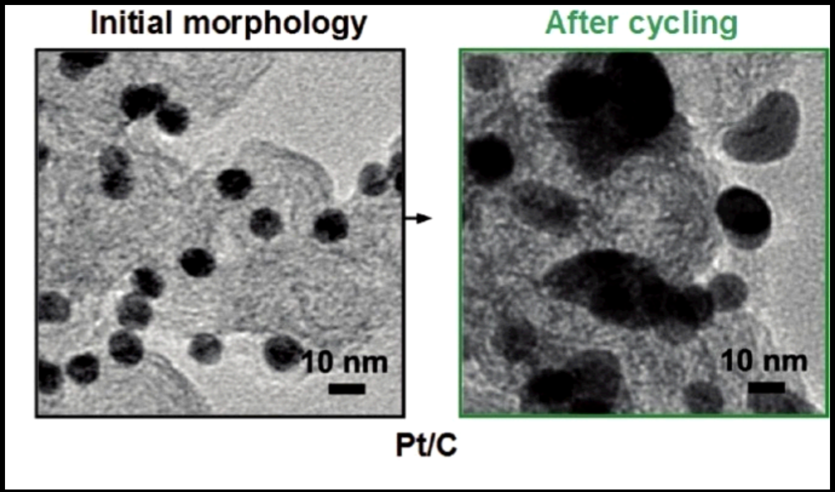
❑ **Slow kinetics for ORR**

- Mass activity: ~0.11 A/mg
- Specific activity: ~0.2 mA/cm^2

❑ **Durability**

❑ **2020 DOE Technical Targets**

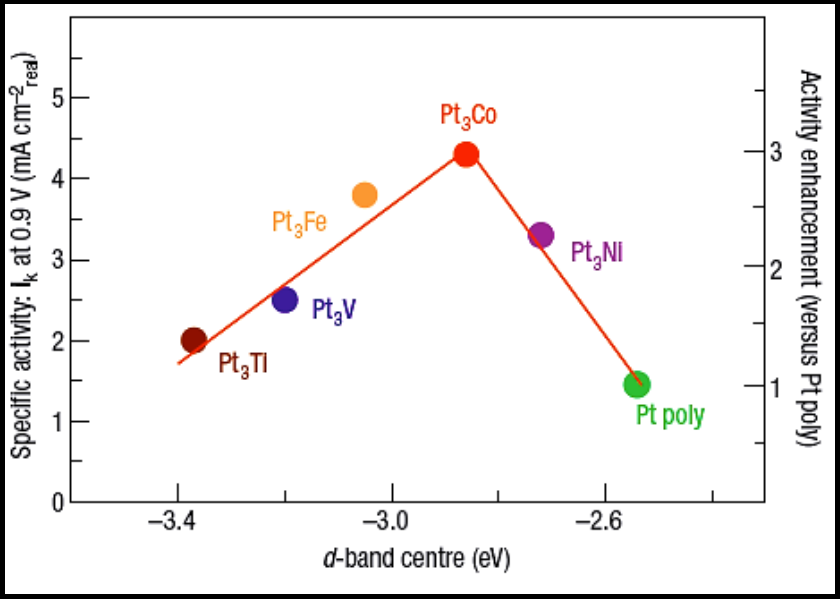
- Mass activity@ 0.9 V: ~0.44 A/mg
- Specific activity @ 0.9 V : ~0.72 mA/cm^2
- Electrochemical area loss: < 40%
- Catalyst support loss: < 30%
- PGM Total loading: 0.2 mg/cm^2 electrode
- Durability w/cycling (80 ^{o}C): 5000 hrs
- …



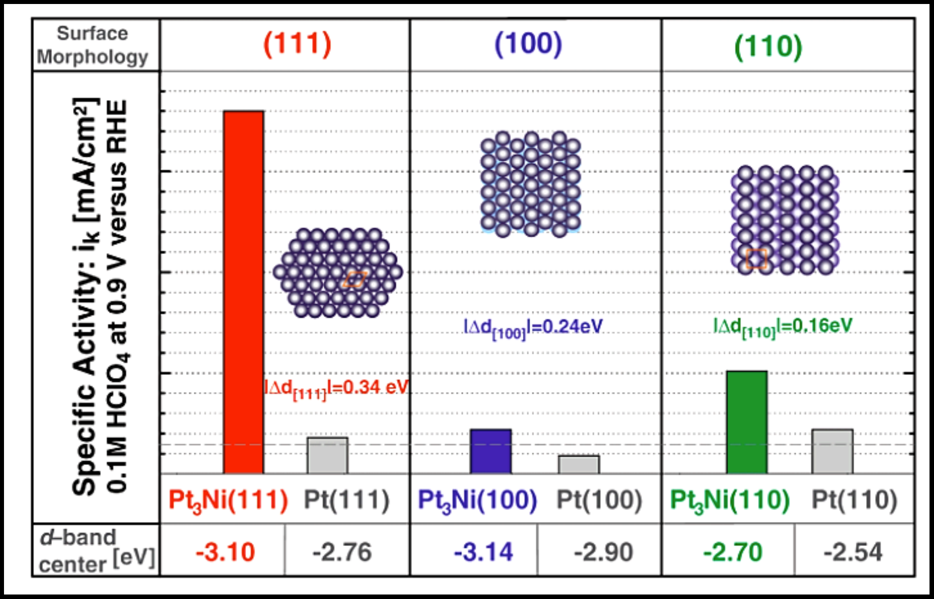
Ref: Wang *et al.*, *Nano Lett.* 11, 919(2011)

Pt-based Multimetallic Catalysis

Alloying/Core shell



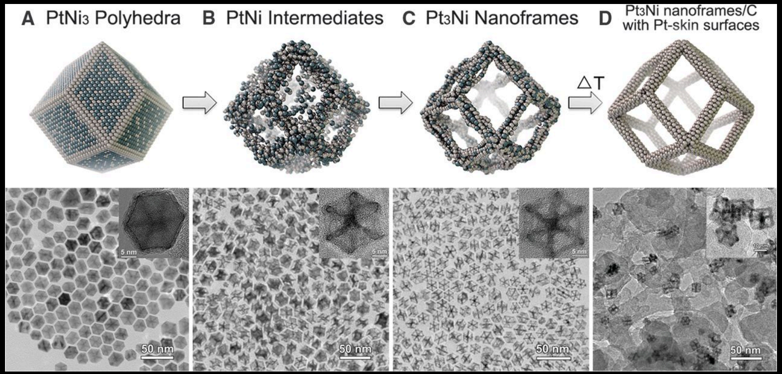
Shape control



Ref.: Markovic *et al.*, *Nat. Mater.* 7, 241,(2007)
Markovic *et al.*, *Science*, 315, 493,(2007)

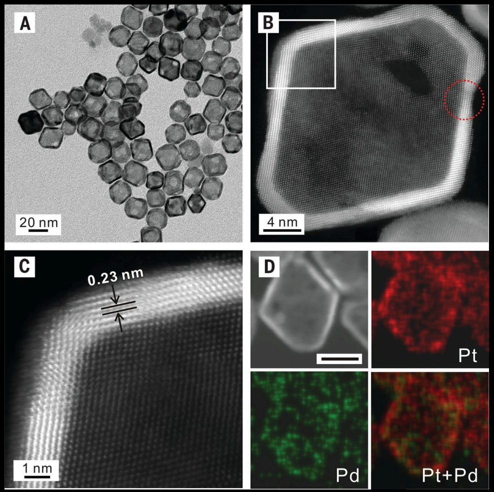
Optimization of Nanostructures

A: PtNi nanoframes



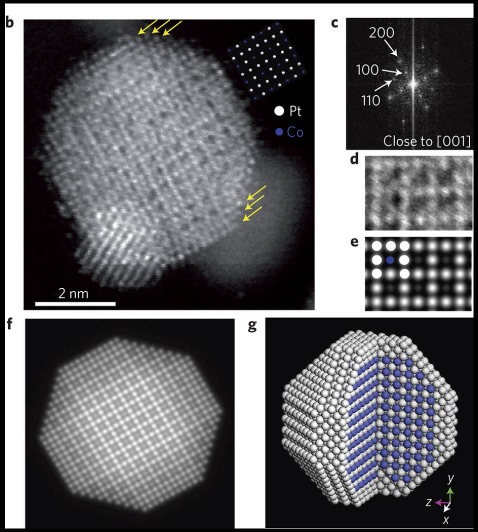
Yang and Markovic 's groups, *Science* 2014, 343, 1399

B: PtPd Nanocages



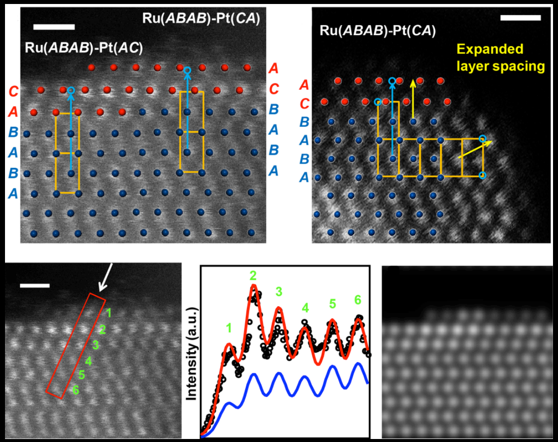
Y. N. Xia's group, *Science* 2015, 349, 412

C: Ordered structure of Pt_3Co



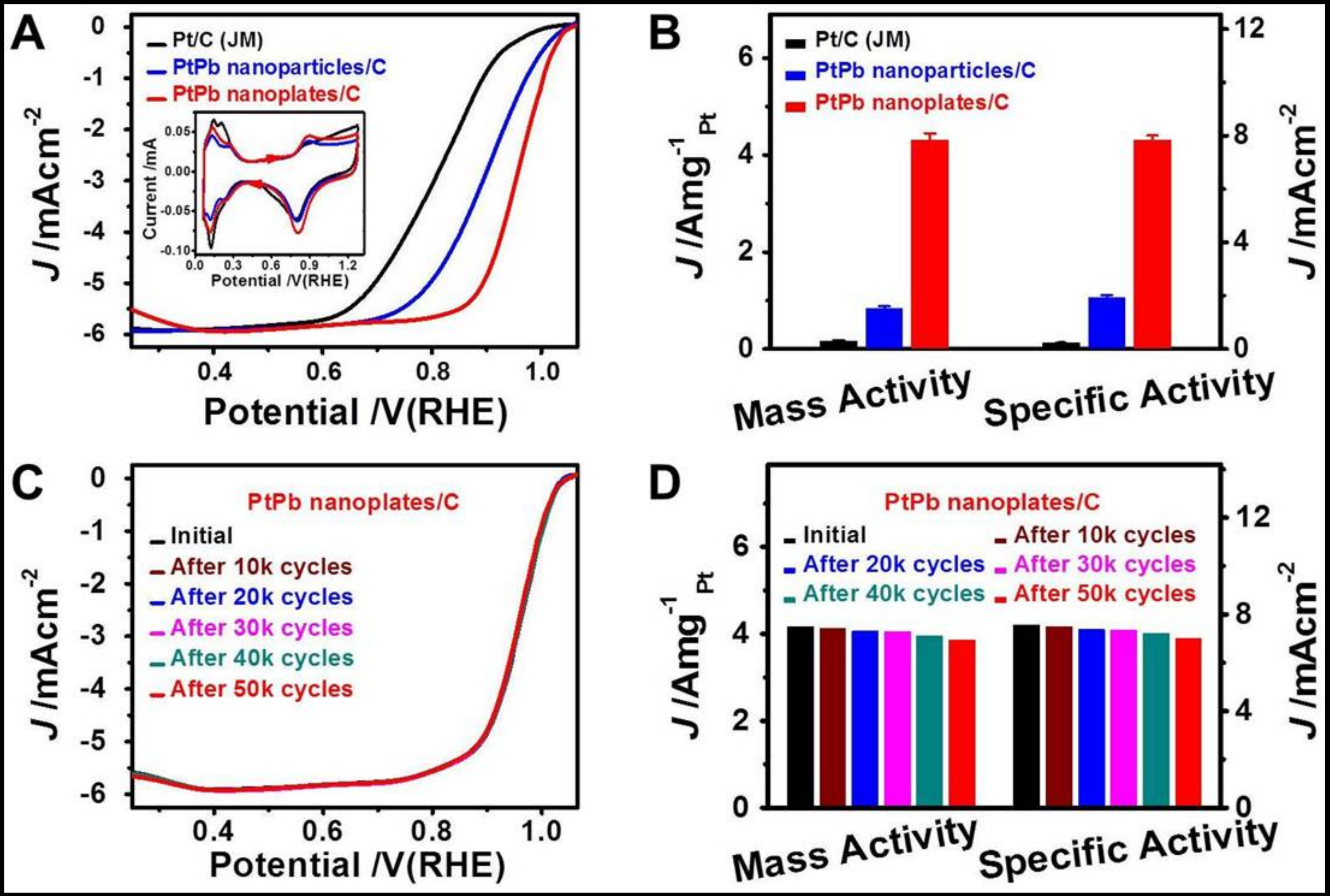
Abruna's group, Nature Materials, 2013,12,81

D: Stacking sequence of Pt(fcc)-Ru(hcp)



With Jia Wang and R. Adzic, Nature Comm., 2013,4,2466

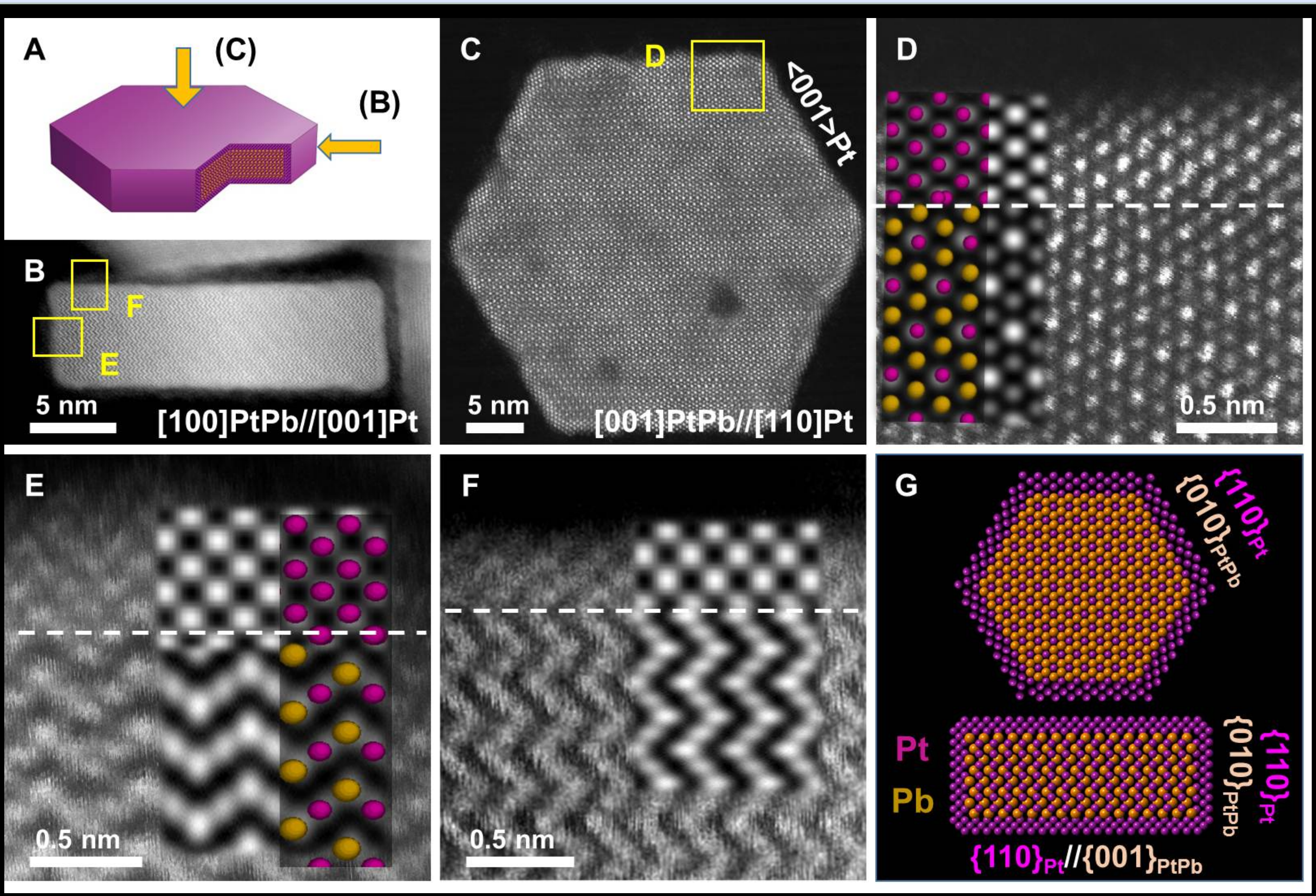
PtPb-Pt Core-Shell Plate for ORR



- Excellent activity and stability! But why?

Synthesis and Electrochemical results by Huang's and Guo's groups

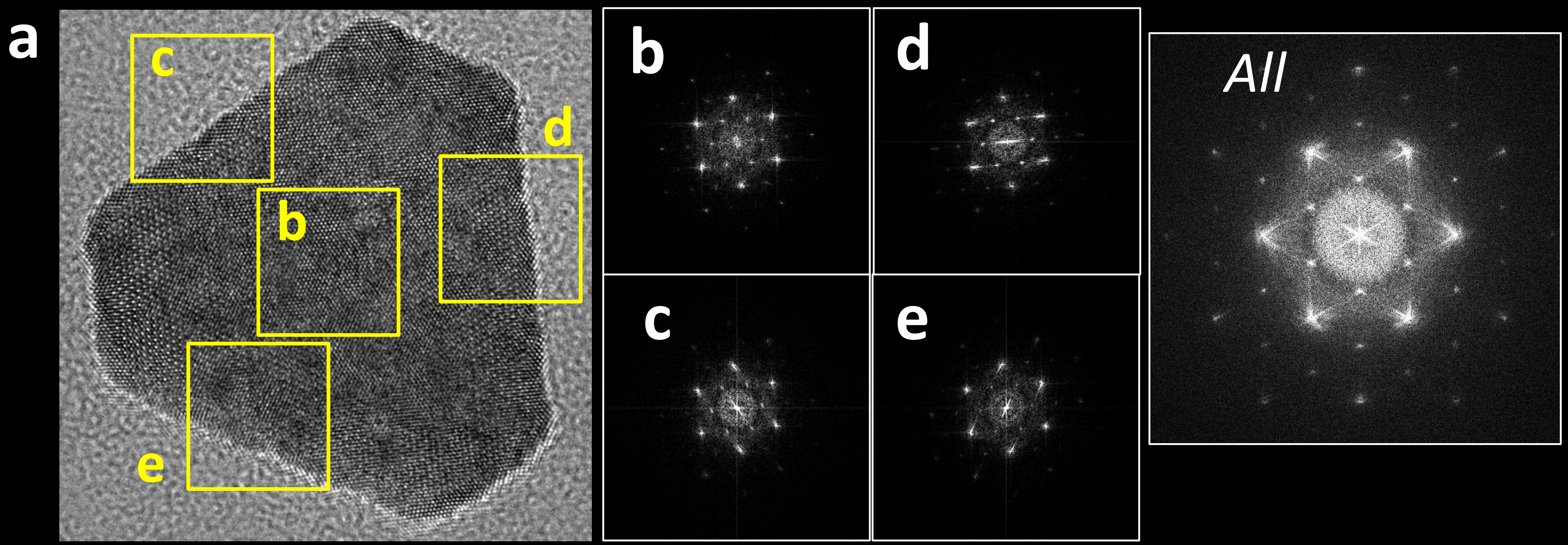
PtPb-Pt core-shell Nanoplate : Hexagonal@Fcc



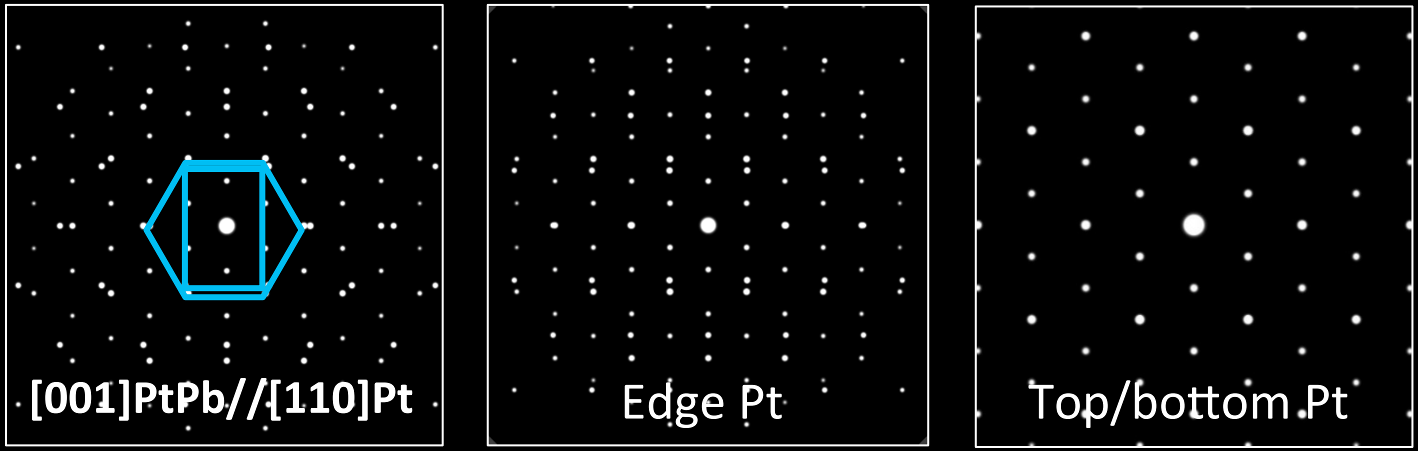
- Core: PtPb/HCP vs Shell: Pt/FCC
- Interfacial coherence:
- Surface Pt and edge Pt
- Corner dislocations

Strain Analysis from Diffraction Patterns

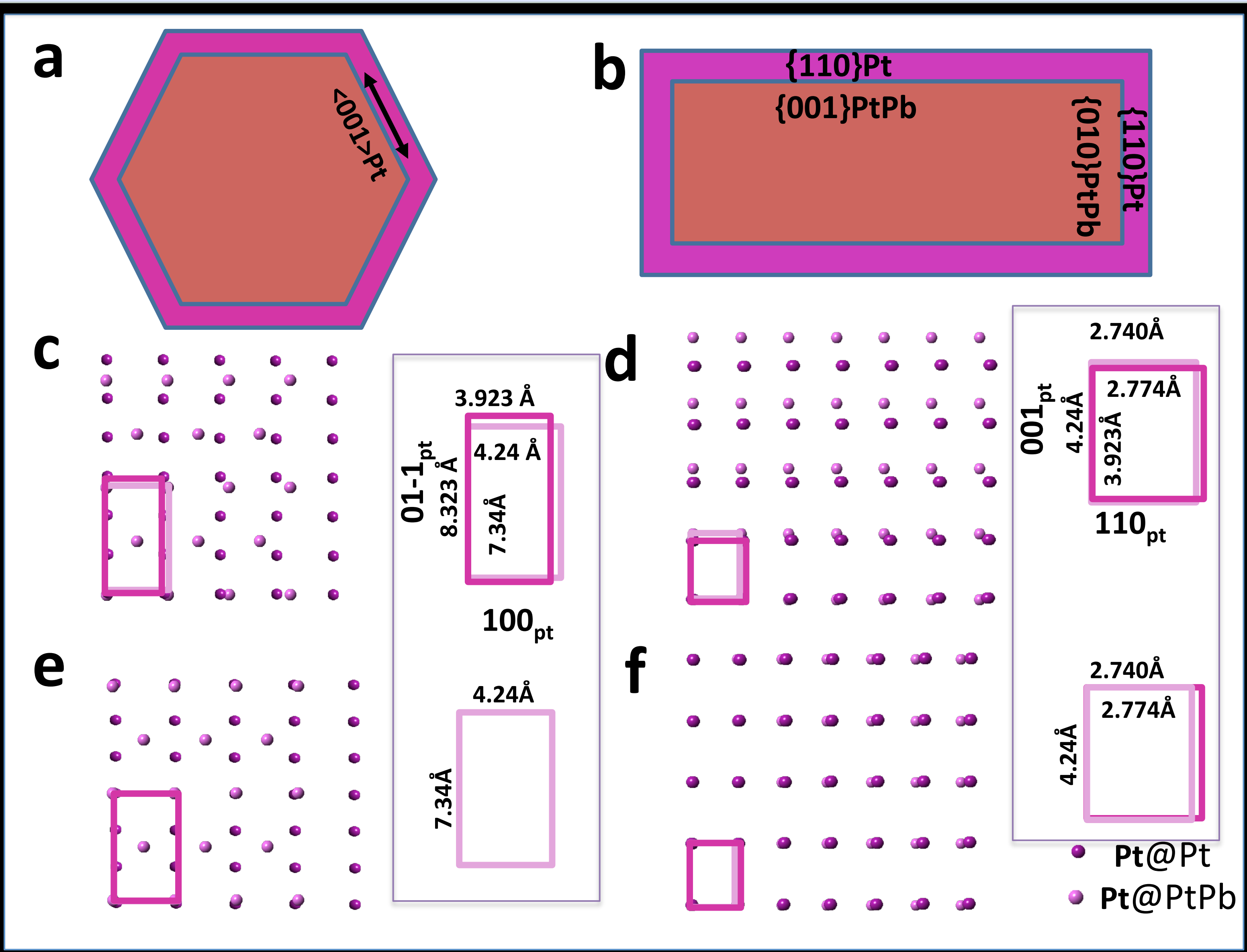
Experimental results(FFT)



Simulations

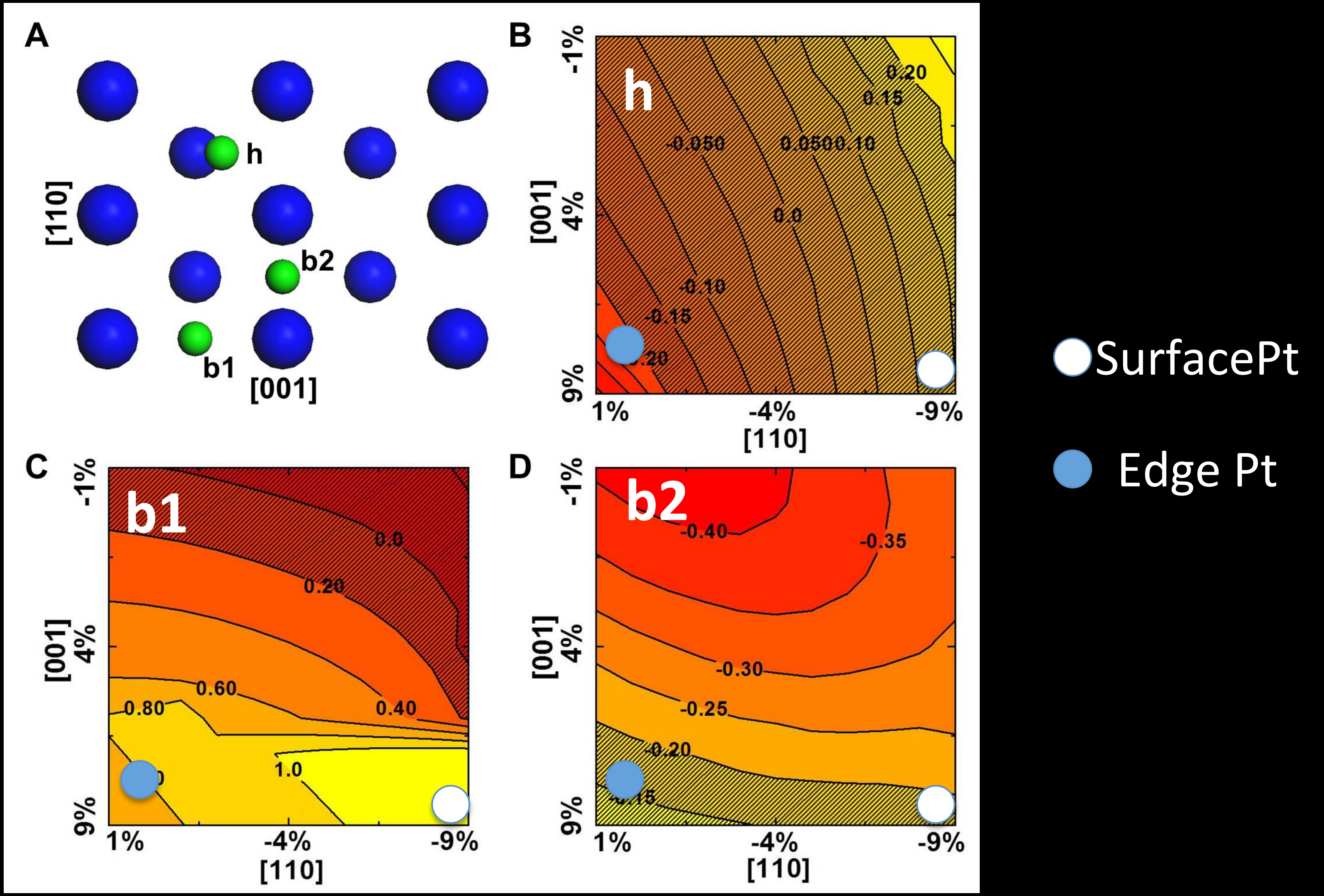


PtPb-Pt Core-Shell: Biaxial Strain



Guo, Su, Huang et al. Science 354,1410(2016)

DFT Calculation: Binding Energy and Strain



DFT calculation by Xu zhang and Gang Lu

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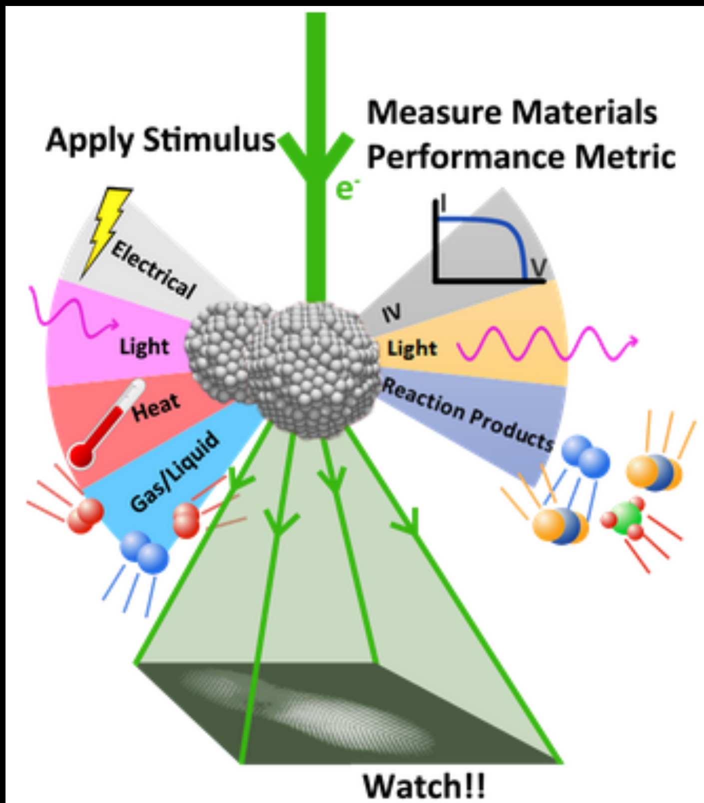
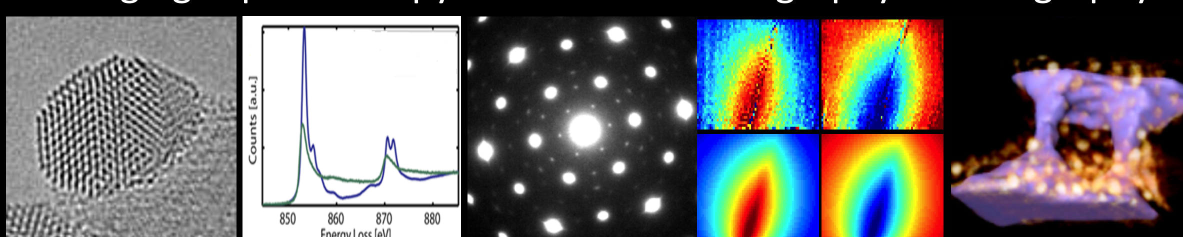
Outlook on In-situ/Operando TEM



- To reveal real-time and spatially-resolved morphological, structural, chemical, and electronic state evolutions during physical and chemical processes.
- To probe direct material response to multiple stimulus applied to the nanoscale system.
- To combine complimentary methodologies simultaneously and at various relevant length scales, enabling information acquisition in extra dimensions.

Imaging Spectroscopy Diffraction Holography Tomography



Ref. H. Zheng et al., MRS Bulletin, 2015

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Thank you for your attention, 谢谢