MBA Lattice Upgrade: New Opportunities for *In-situ* High Energy (30 keV – 90 keV) X-ray Structural Analyses

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Argonne National Laboratory

Workshop on New Science Opportunities Provided
by a Multi-bend Achromat Lattice at the APS
October 21 & 22, 2013

Structural Analyses Using In-Situ High Energy (30 keV – 90 keV) X-ray Scattering

- Provides New Approach to Critical, High-Impact Science:
  - Solar Fuels
  - Catalysis (chemical energy conversion)
  - Energy Storage (batteries)
  - Materials Chemistry
- Large User Community
  - Committed DOE/International Energy Research Communities
  - DOE-Hubs (JCAP, Battery), EFRCs (ANSER, IACT, …)
- Distinguishing Capability for APS Among U.S. Light Sources
  - Highlight point in competition for next generation storage ring

MBA Lattice Upgrade, New Opportunities:

- **Solar Fuels and Electrochemical Energy Conversion**
- **Structural Analyses Using In-Situ High Energy (30 keV – 90 keV) X-ray Scattering**

Example: “Artificial Leaf” / Solar Fuels Technology

- High-Priority, National/International Needs Research
- Fundamental Research:
  - Complex Chemistry, Heterogeneous Catalysts, Interfacial Processes
- Applied Research:
  - Device Physics, In-situ Analyses, Prototype Studies
- Structure Underlies Discovery of Chemistry for Sustainable Energy

Challenges for Solar Fuels Science/Technology

- Interfacial thin films (≤ μm)
- Catalysts = Amorphous films / crystalline defect materials / molecular
- Spatially inhomogeneous
- Structure, Assembly, and Catalytic Mechanisms Unknown

Opportunities from MBA Lattice Storage Ring:

- Collimated, μm (< μm, focused) high energy X-ray beam:
  - *In-situ* thin-film X-ray structure characterization for atomic scale structure (pair distribution function, PDF analysis)
  - Local spatial resolution/mapping of structure/chemistry within catalyst films
- High flux, brilliance:
  - High-throughput data acquisition:
    Path for new materials discovery, *eg.,* structural analyses coupled to combinatorial syntheses:
  - Dynamics\Time-resolved characterization:
    Path to discovery of 1st principles and rational design of new materials, *eg.,* follow assembly and catalytic reaction mechanisms:

Amorphous, electrochemically-deposited water-splitting catalysts. Two examples:

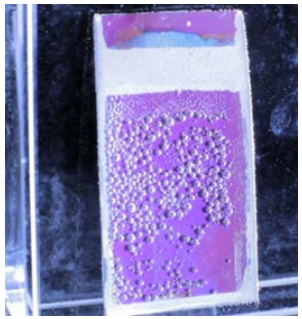
❑ Cobalt-phosphate Water-oxidation Catalyst

Kanan & Nocera *Science*, 2008, *321*, 1072.

Solution precursors:

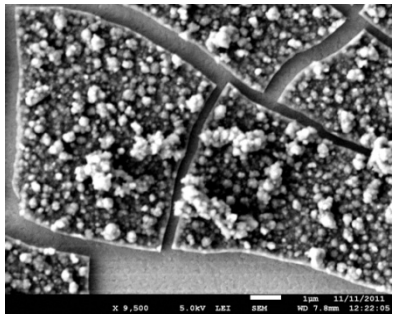
$Co(NO_3)_2$
+
$KHPO_4$, pH 7

Oxidation



Artificial Leaf

Nocera et. al., *Science* 2011, 334, (6056), 645-648



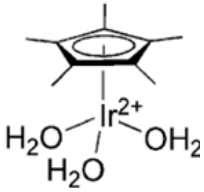
SEM

Pingwu Du and CNM, ANL

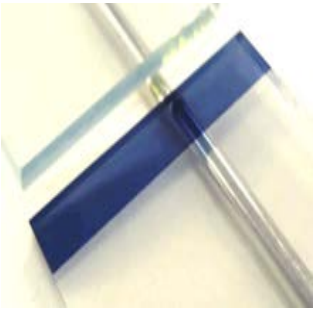
❑ Amorphous Iridium Oxide Water-oxidation Catalyst

Blakemore, Brudvig, Crabtree *et al.* (2011) *Chem. Sci.* 2, 94.

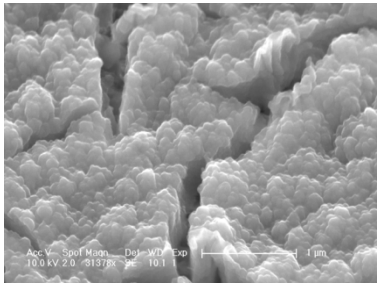
Solution precursors:



Oxidation



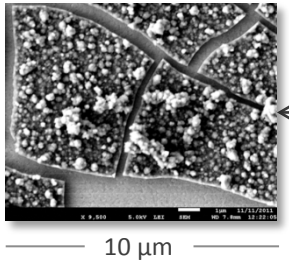
Highly active water-splitting catalyst amorphous film ($0.45 per ft²!)



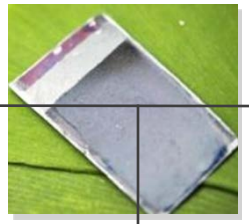
SEM

Andrew Winter, YALE

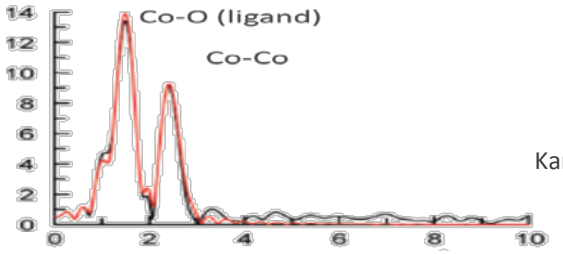
Amorphous Co-Pi OEC Catalyst Film Structure



SEM



XAFS

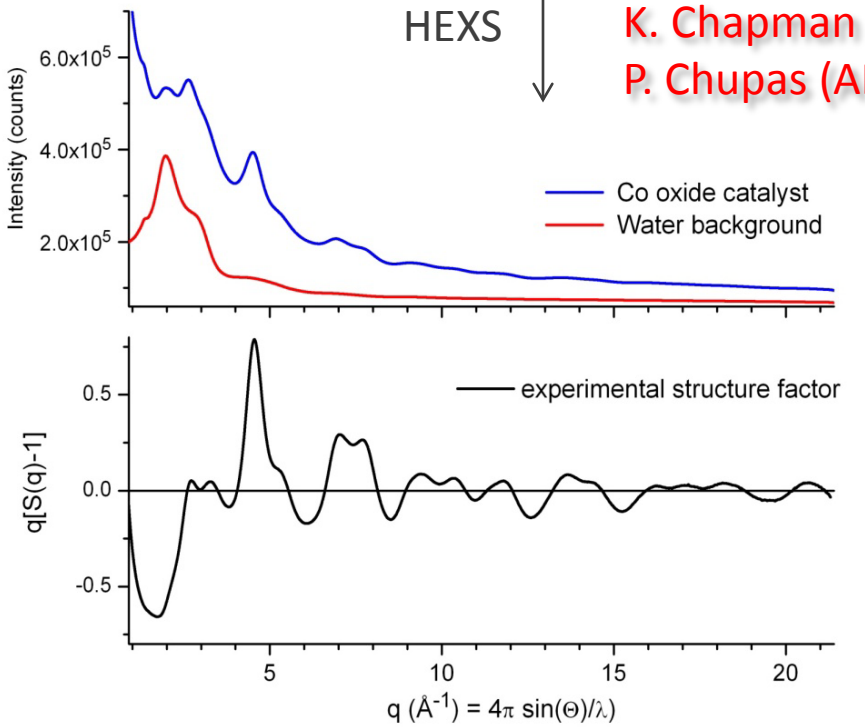


XAFS

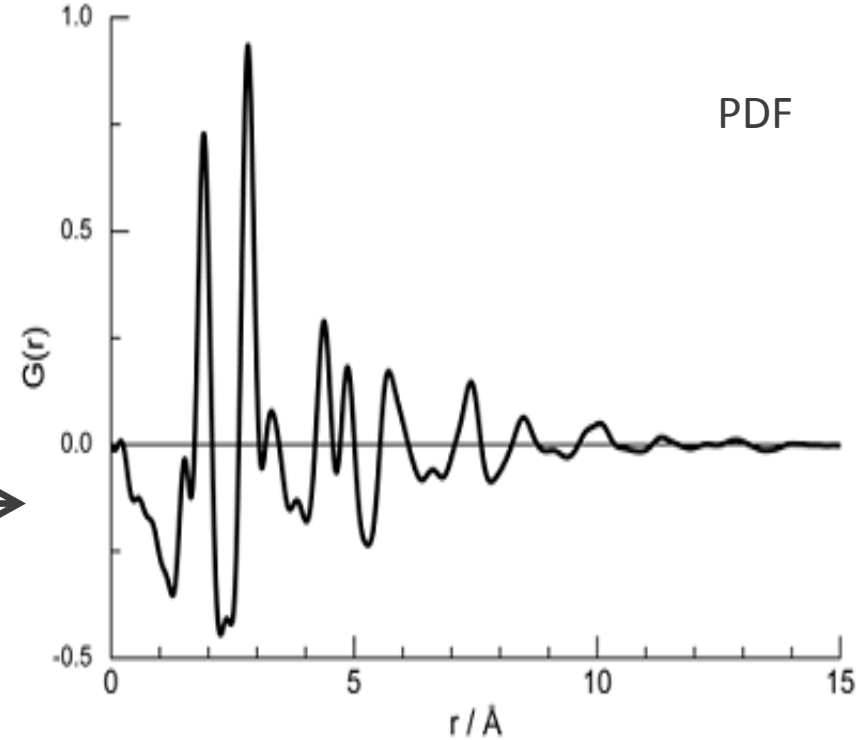
Kanan, et al, JACS 2010
Et al., Dau, JACS 2009

HEXS

K. Chapman (APS)
P. Chupas (APS)



FT



Du, Kokhan, Chapman, Chupas, Tiede, *JACS* (2012) ***134***: 11096

- **High resolution (0.1 Å) atomic pair correlation**
- **Multi-scale 0 Å to 100s nm**
- **PDF probes another length scale- Fills gap between XAFS and SEM**

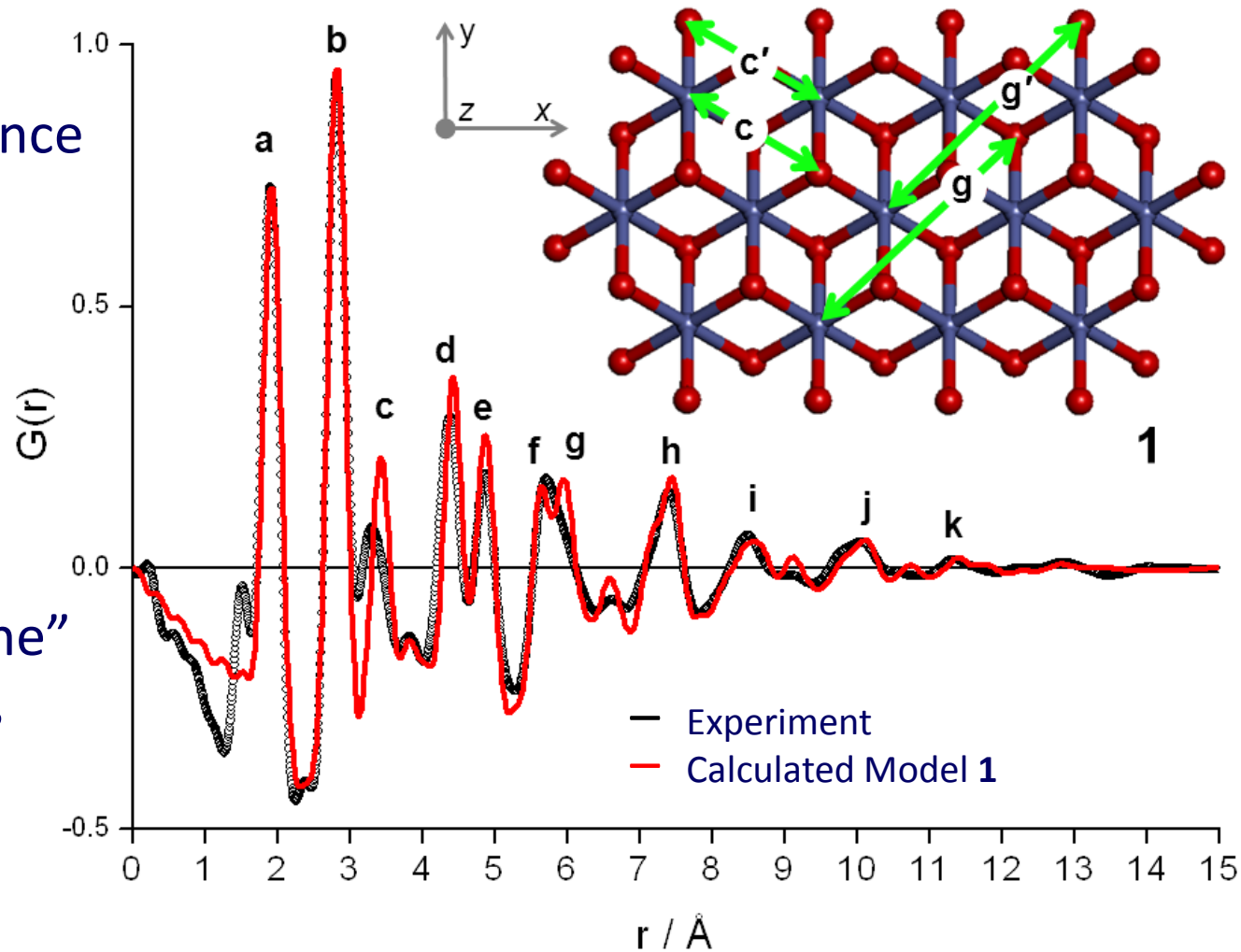
Comparison Experiment and Model PDF for Co-Phosphate OEC Film

Single layer, 13-14 Co atom, “edge-sharing” cobaltate lattice domain model:

PDF Pattern, Distance Decay Reflect:

Domain

- Structure
- Size
- Aspect ratio
- Rule out “cubane” domain models



Du, Kokhan, Chapman, Chupas, Tiede, *JACS* (2012) ***134***: 11096–11099.

Opportunity for model refinement based on PDF

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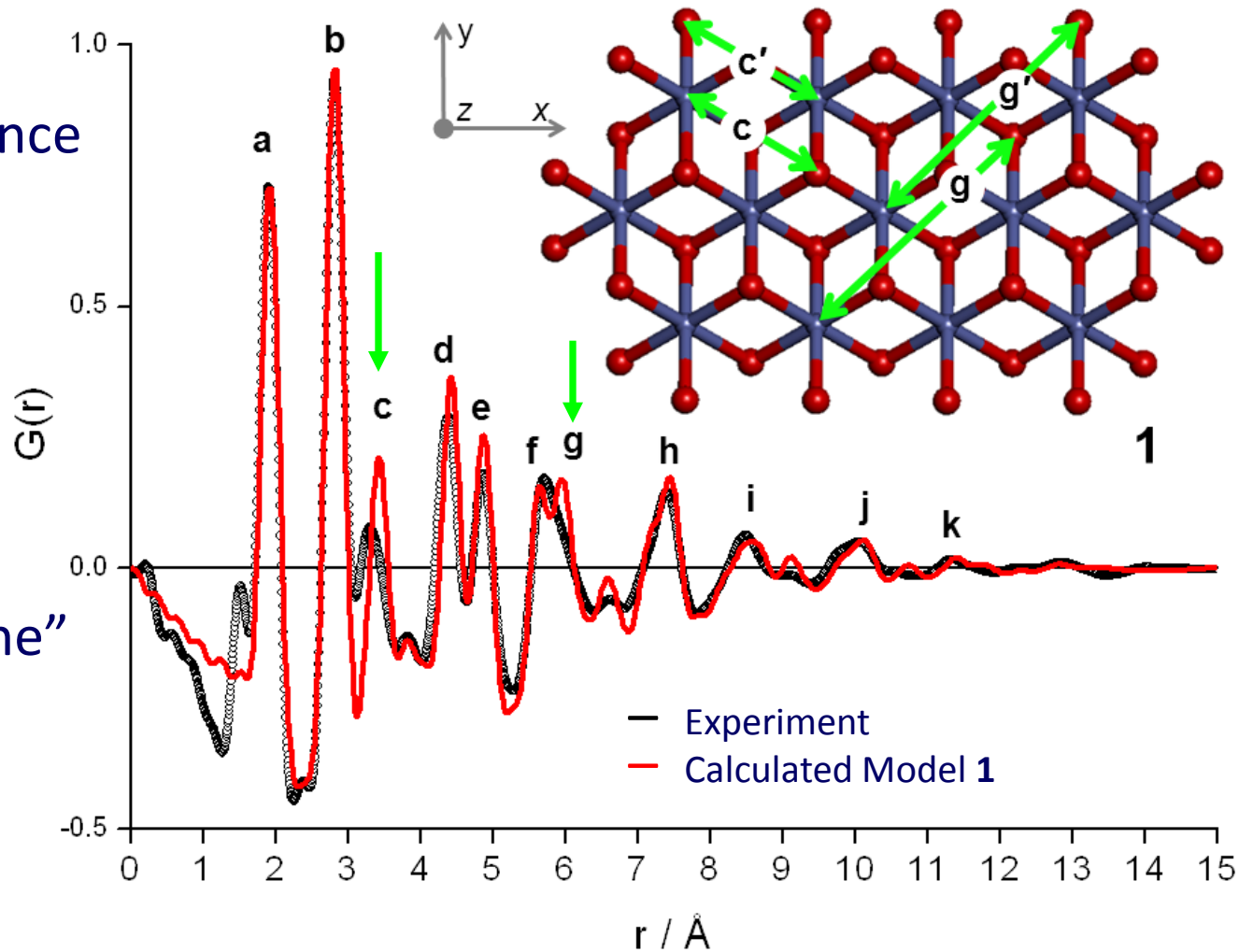


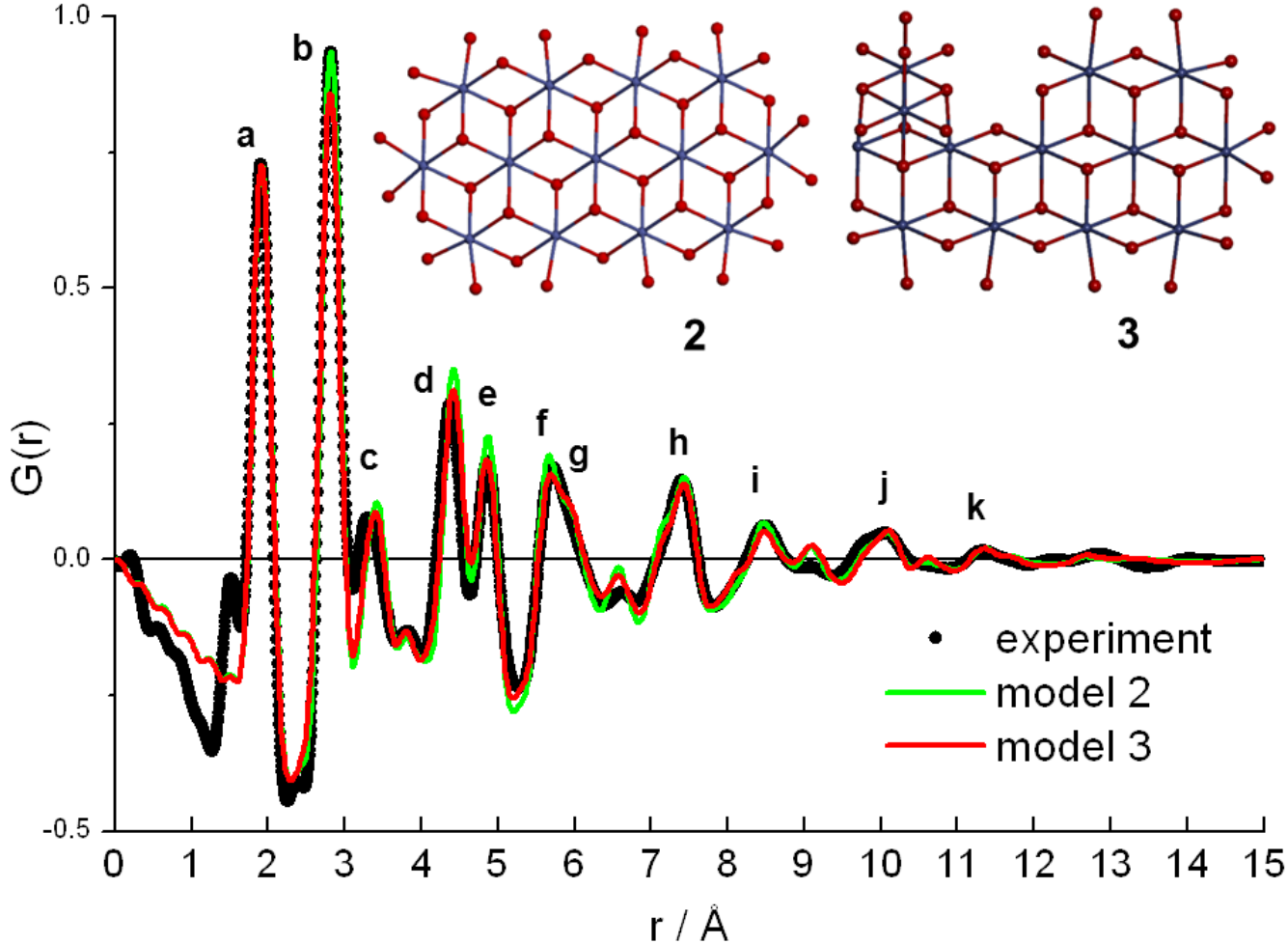
Du, Kokhan, Chapman, Chupas, Tiede, *JACS* (2012) ***134***: 11096–11099.

PDF Guided Structure Refinement

Single layer, 13-14 Co atom, “edge-sharing” cobaltate lattice domain models:

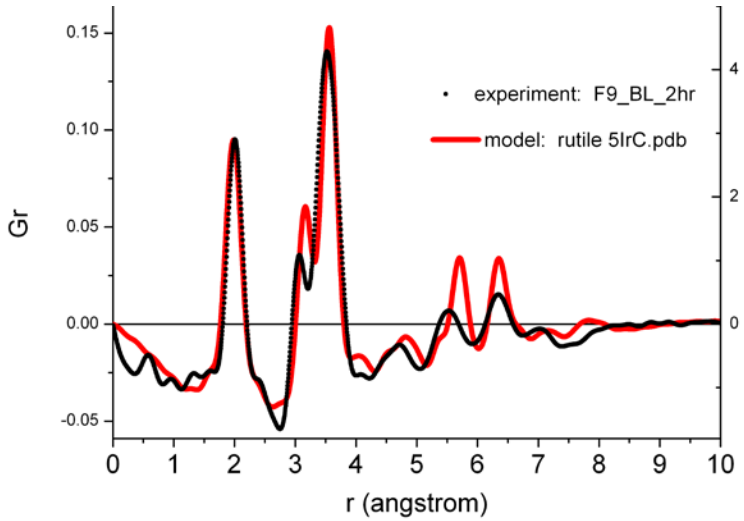
- 13-14 Co atom cobaltate , octahedral CoO_6, lattice domain
- Defect sites, eg., single cubane inclusion

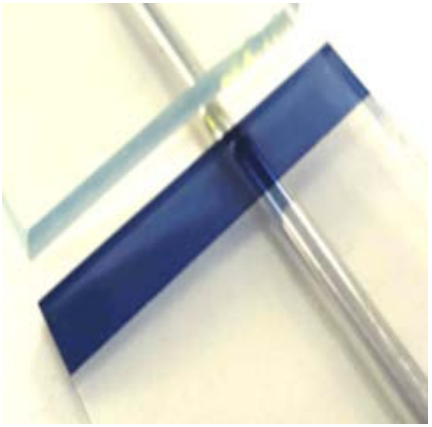
These distortions from crystalline structure improve fits to data



Du, Kokhan, Chapman, Chupas, Tiede, *JACS* (2012) ***134***: 11096–11099

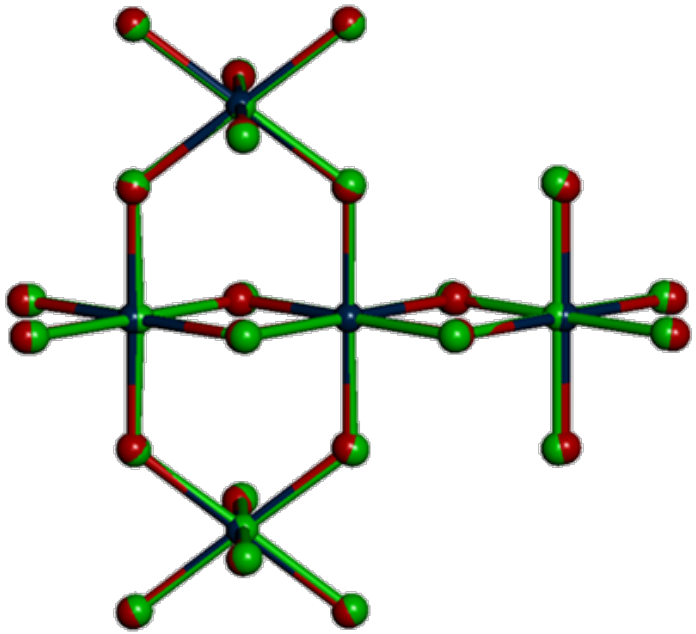
Refining the model based on PDF data



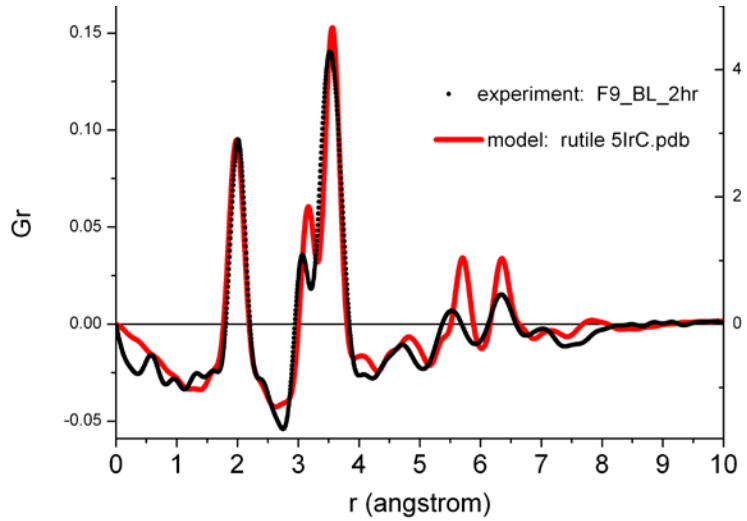


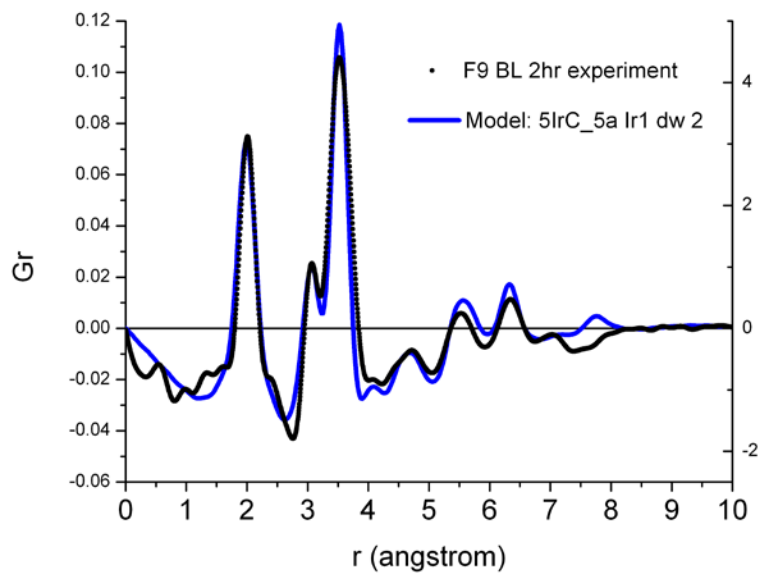
Starting Model

Refined Model



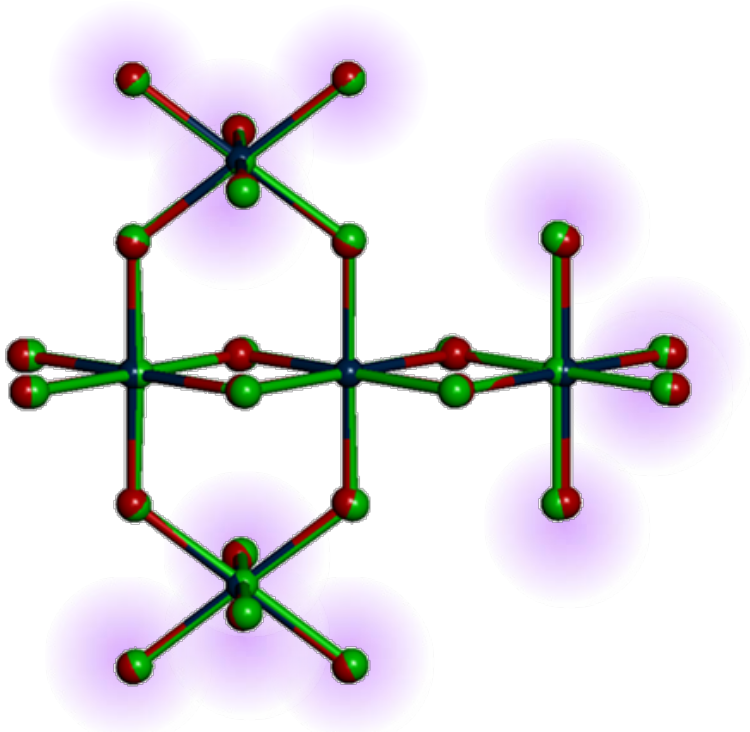
Refining the model based on PDF data





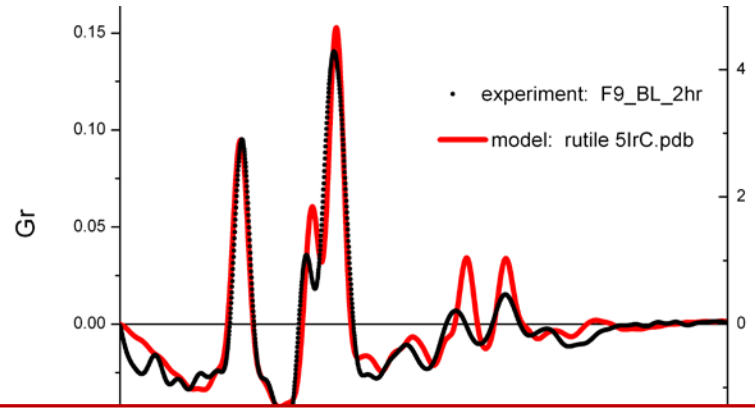
Starting Model

Refined Model

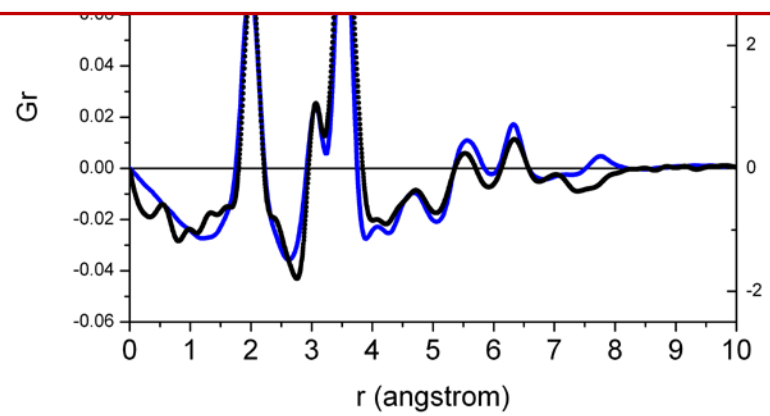


= Debye-Waller factor

Refining the model based on PDF data

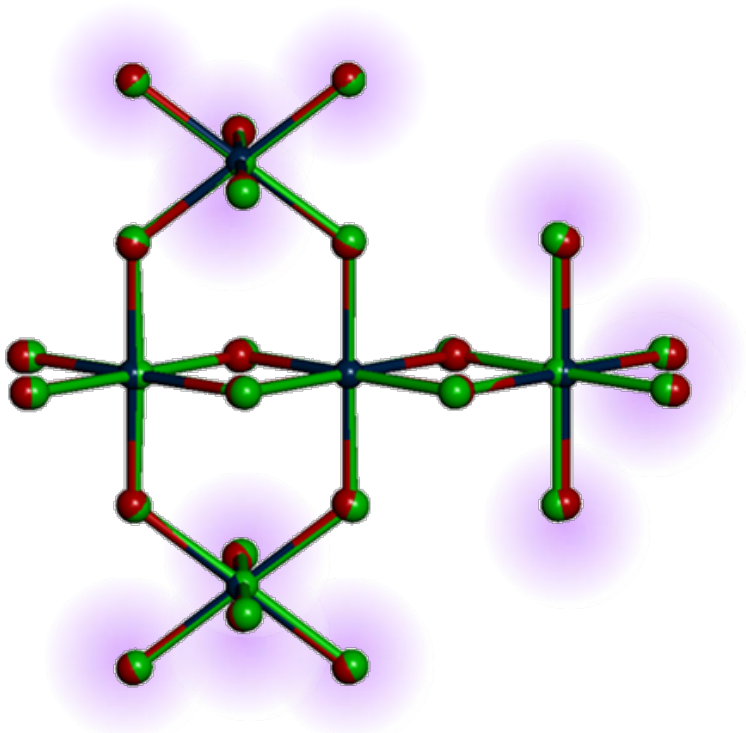


Illustrates ability for PDF to resolve sub-angstrom structure change linked to catalytic function



Starting Model

Refined Model



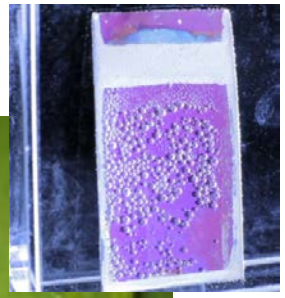
= Debye-Waller factor

“Artificial Leaf” Technology

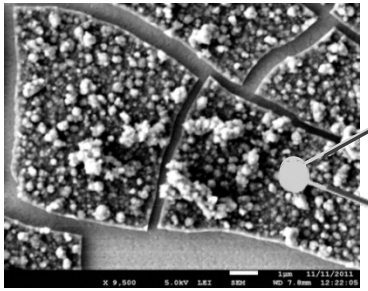
Solar Fuels, Water-Splitting Catalysts Electrochemically-Processed from Small Molecule Precursors

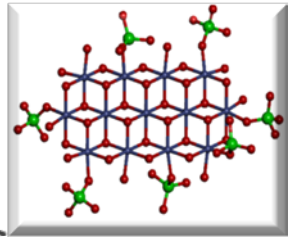
→

Combined X-ray spectroscopy/PDF Analysis: “Auxiliary” Ligands Provide Biomimetic Function

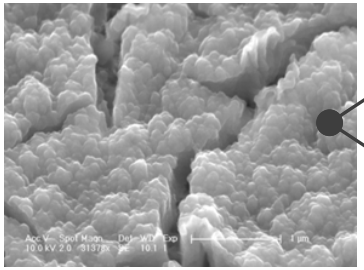


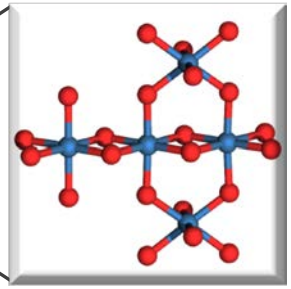
Nocera (MIT/Harvard)





Cobalt-oxide/phosophate amorphous film

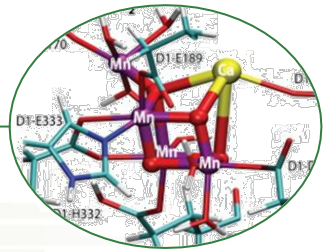




Iridium-oxide amorphous film

G. Brudvig, R. Crabtree (Yale)

Photosynthetic Water-splitting $CaMnO_4$ cluster



PDF Detection of Structural Dynamics- Correlation to Function

Newton, Chapman, Thompsett, Chupas
JACS (2012)134: 5036

Current State-of-the-Art PDF:

- Resolution of Pt-Pt spacing within surface Pt-Ox layer coupled to catalysis
- 1 wt % Pt on Al_2O_3 catalyzing CO oxidation during cyclic "redox" operation.
- Capillary reactor (macroscopic)
- Seconds timescale resolution

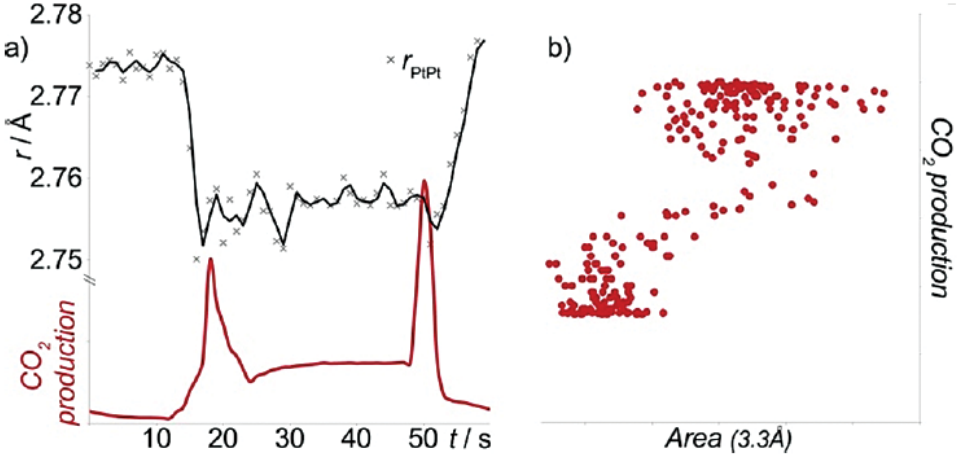


Figure 3. (a) The CO_2 production and average Pt–Pt bond length through a single redox modulation. (b) The steady-state CO_2 production is correlated with the non-fcc feature at 3.3 Å.

Opportunities for MBA Lattice Upgrade:

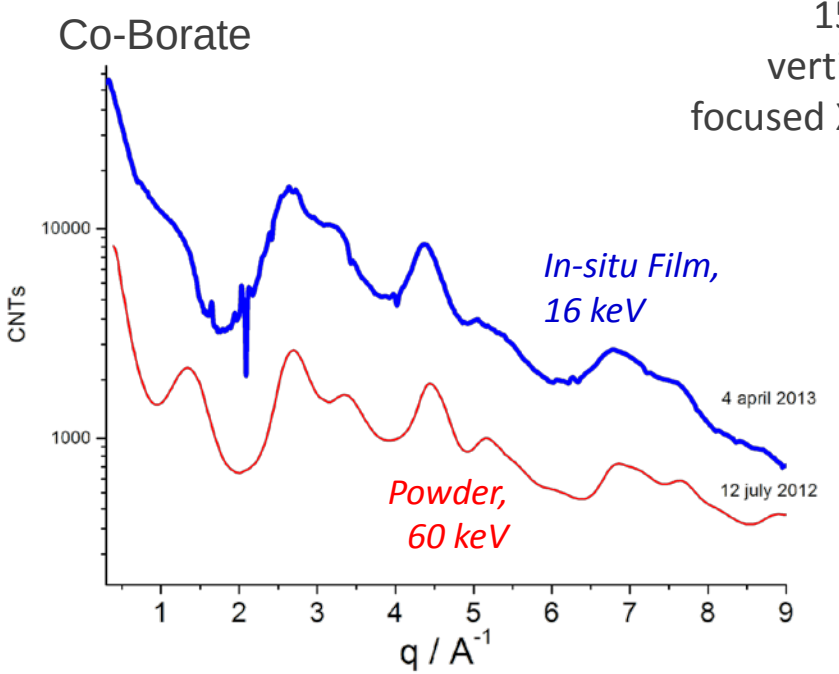
Extend High Energy PDF:

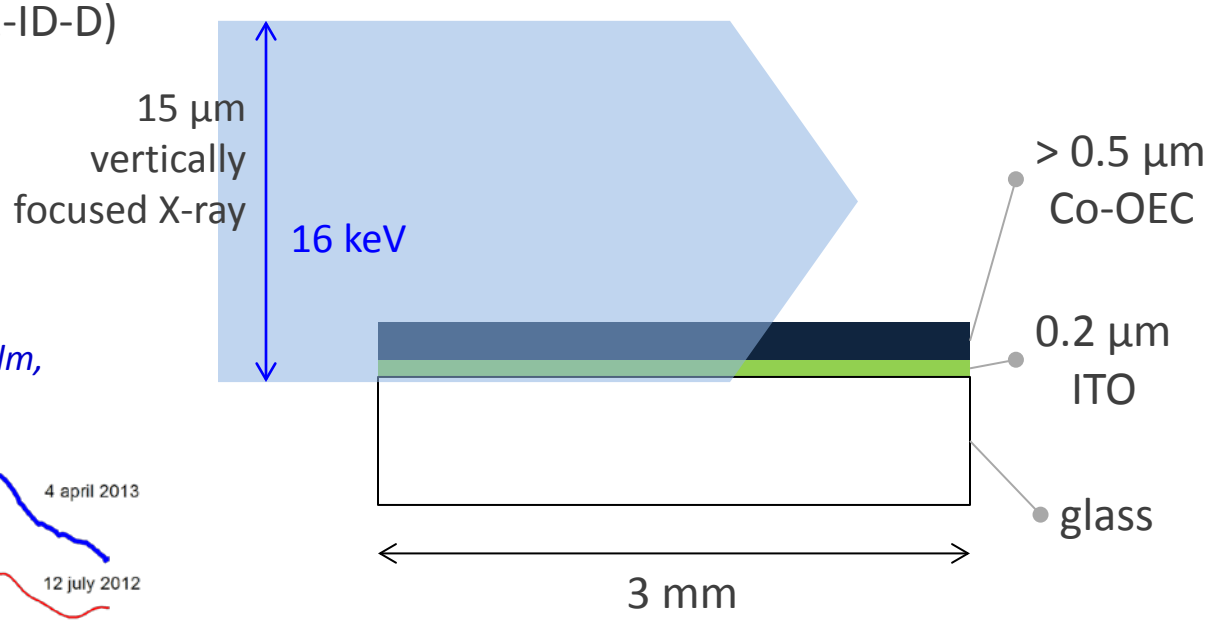
- *In-situ*, interfacial, thin film structural characterization
- Spatial profiling, mapping
- Enhanced time-resolved capabilities
  - Investigation film assembly, repair
  - Catalytic mechanisms
  - Provide structure-based design principles

Present Limitations-
Structures on Electrodes- Solar Device Architectures

- OEC films on planar electrodes

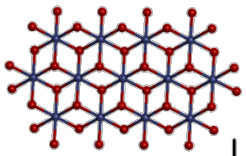
Xiaoyi Zhang (11-ID-D)

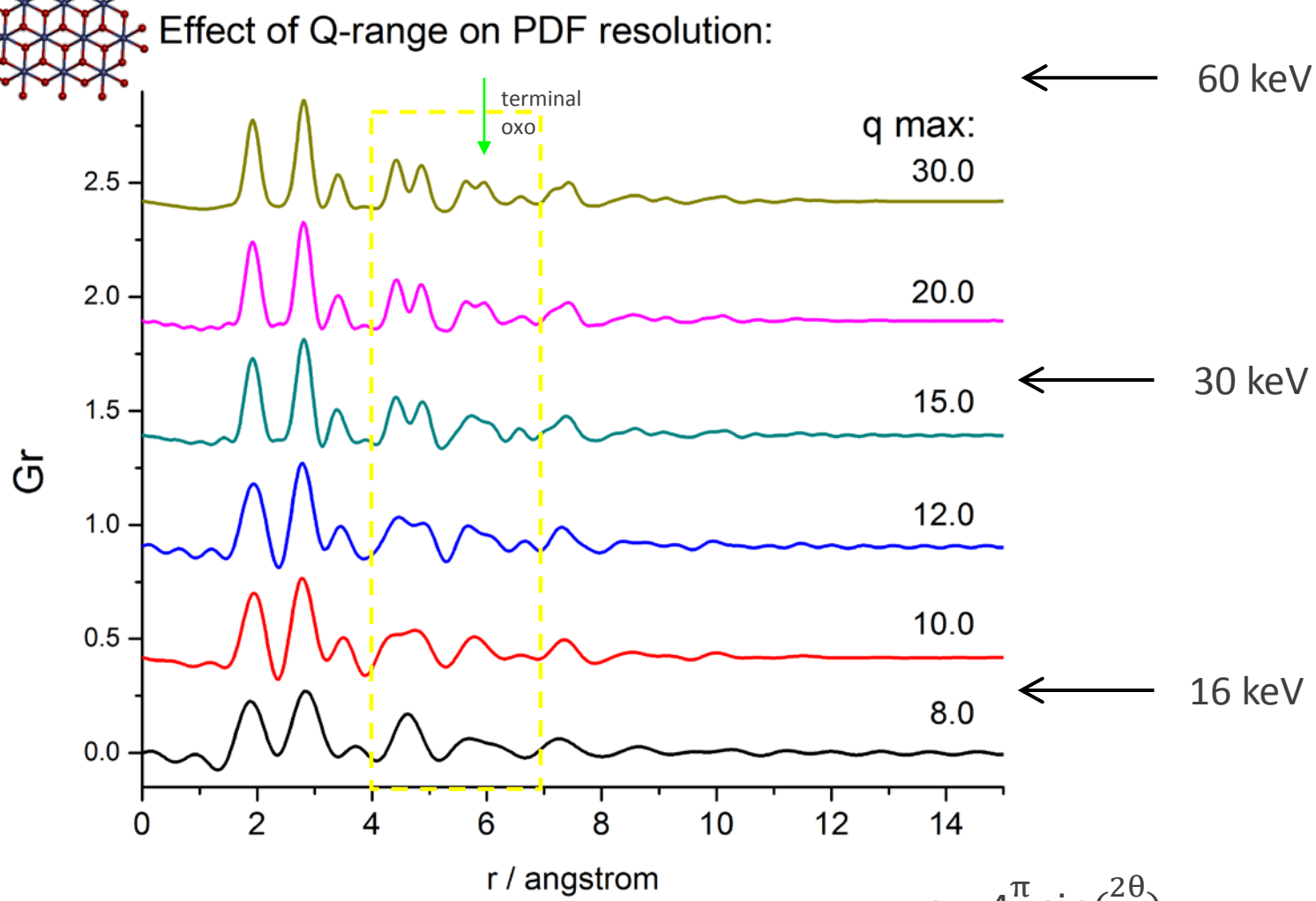




- Resolve x-ray scatting for *in-situ* film when ≥ 0.5 um
- Suggest stacking varies from *ex-situ*
- Not applicable to thin films/ molecules

Atomic Scale, High Resolution Requires High Energies





$$q = 4\frac{\pi}{\lambda}\sin\left(\frac{2\theta}{2}\right)$$

Present Limitations- Structures on Electrodes- Solar Device Architectures

- OEC films on planar electrodes

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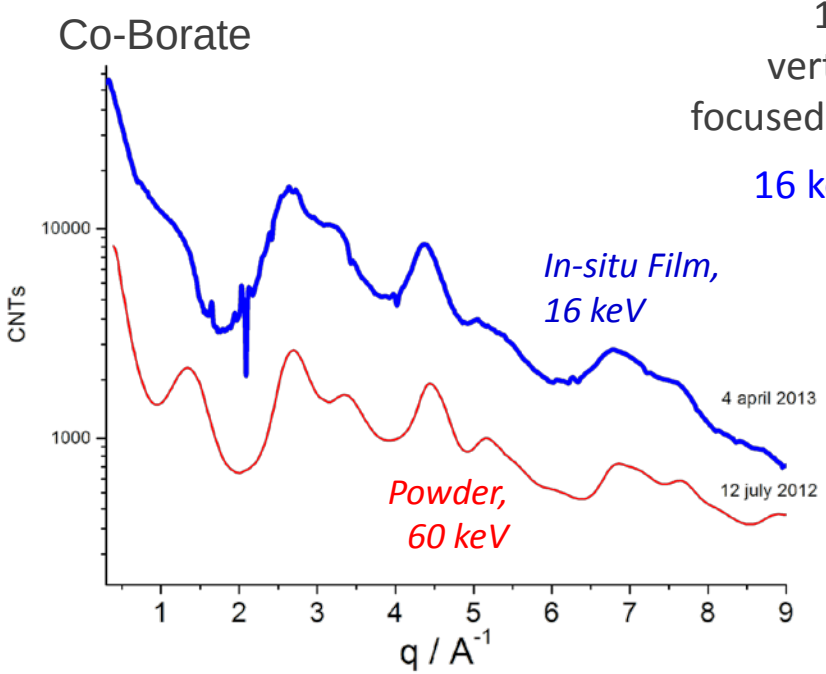

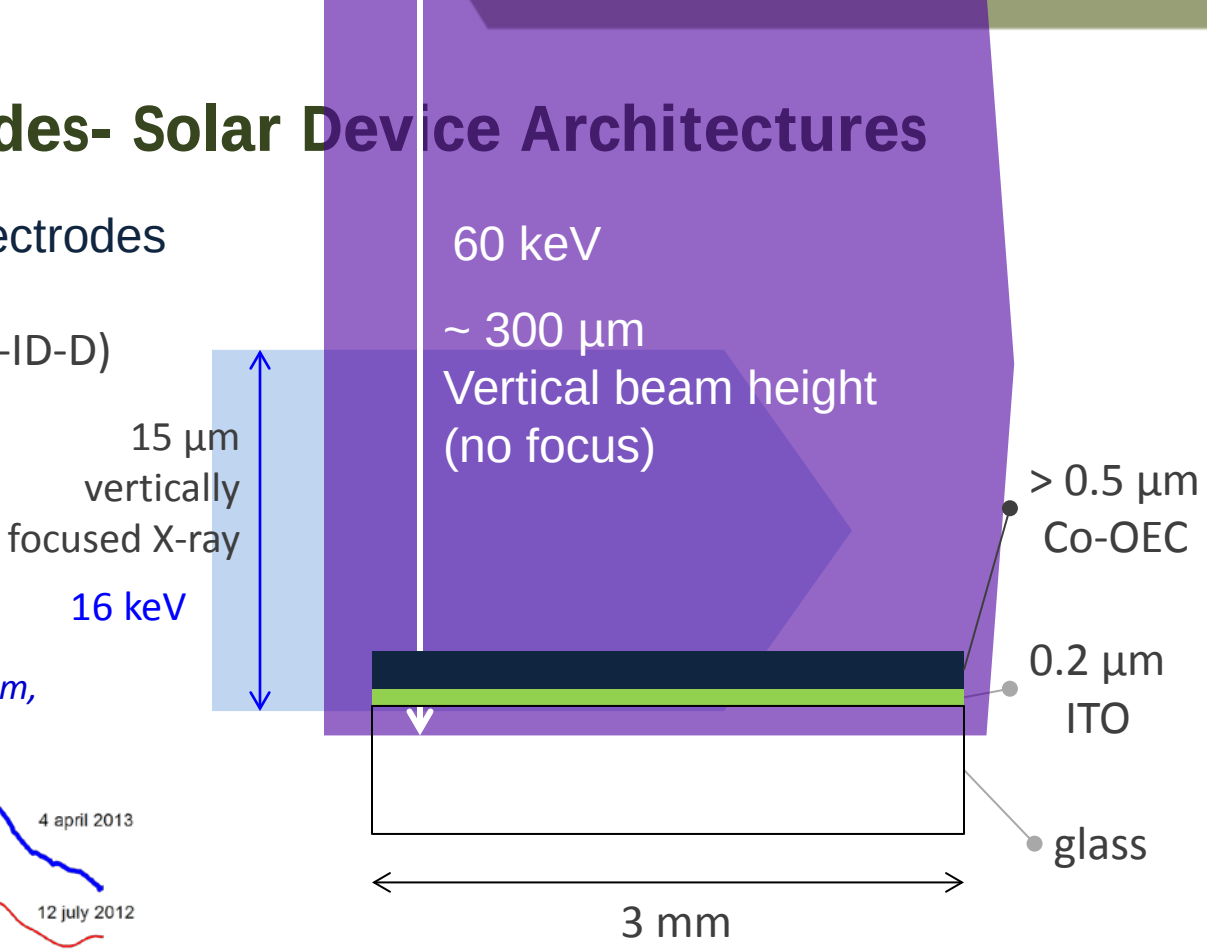

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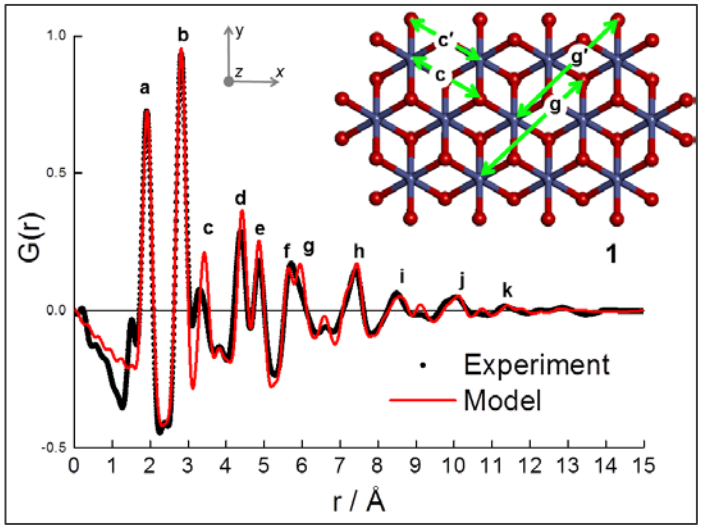
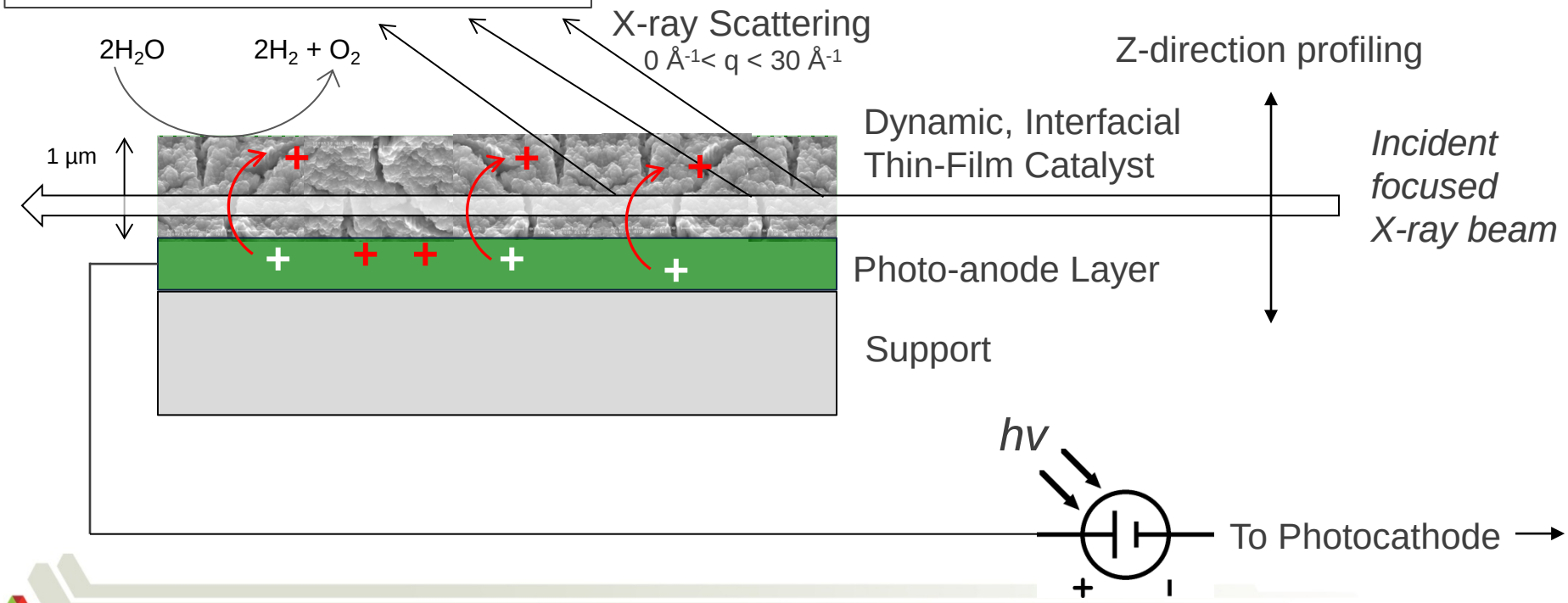
In-situ thin-film solar catalyst device characterization

Atomic Pair Distribution Function (PDF)



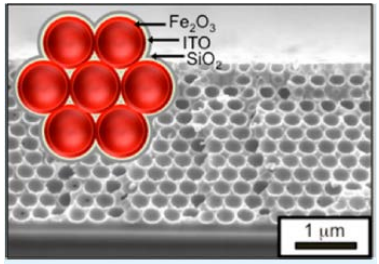
Enabling Capabilities of Ultra Storage Ring Light Source:

- *Coherent, focused high energy X-ray*
- *More useable photons than synchrotron*
- *Spatially profiled structure*
- *High-throughput measurements- combine with combinatorial synthesis*
- *Time-resolved: follow assembly, reaction mechanisms*

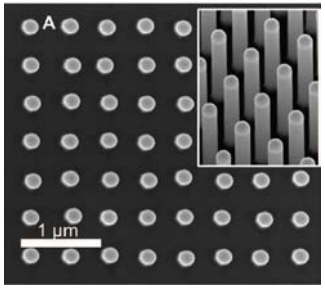


Proposed Work-
Build Thin Layer, Molecular Layer Catalysts on-
Nanostructured Electrodes with Difference PDF

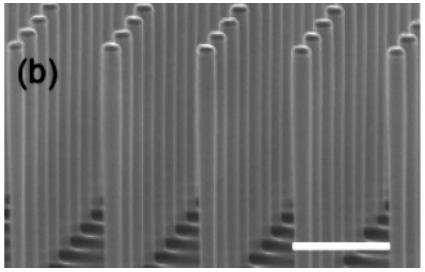
- Micron-scale vertical, nanostructured electrodes



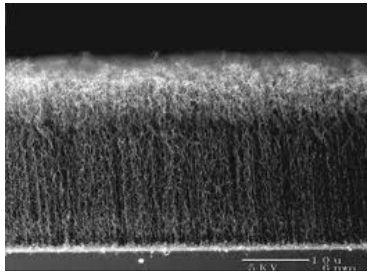
ACS Appl. Mater. Interfaces 2013, 5, 360



Wallentin et al Science 2013

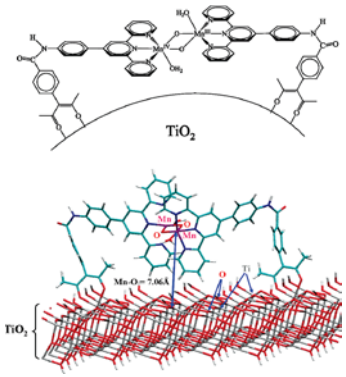


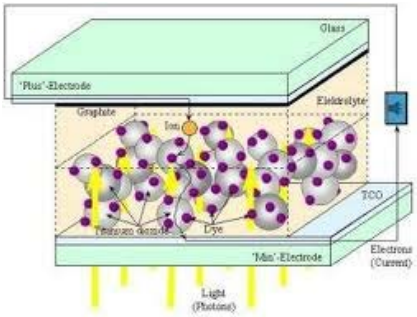
Zhang et al APL 2008

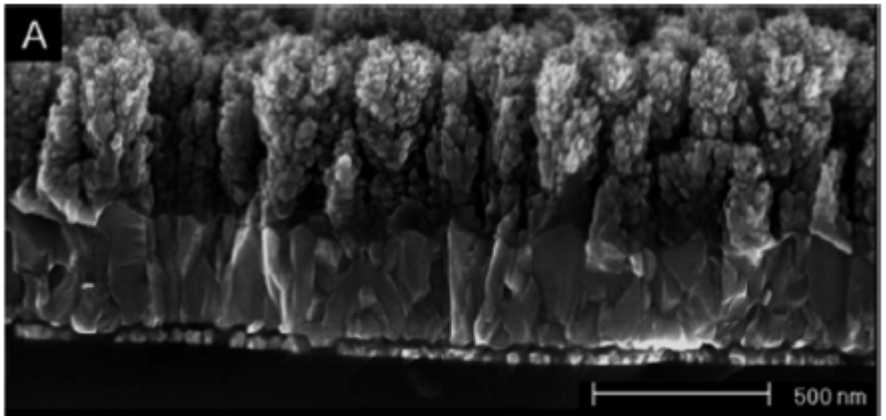


InP Silicon Carbon nanotubes

- Semiconductor nanoparticles- structured semiconductors







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