HTE team:
J. Gregoire (PL),
J. Jin (co-PL), M. Marcin, S. Mitrovic, E. Cornell, C. Xiang, E. Soedarmadji, S. Suram, K. Kan, J. Haber, P. Newhouse, D. Guevarra, R. Jones, N. Becerra, M. Pesenson, L. Zhou, A. Shinde

Affiliates:
E. McFarland, N. Lewis

A HIGH THROUGHPUT EXPERIMENTATION PIPELINE FOR THE DISCOVERY OF SOLAR FUELS MATERIALS

John Gregoire, HTE Project Lead

LBNL Interdisciplinary Instrumentation Colloquium, 30 Sept 2015

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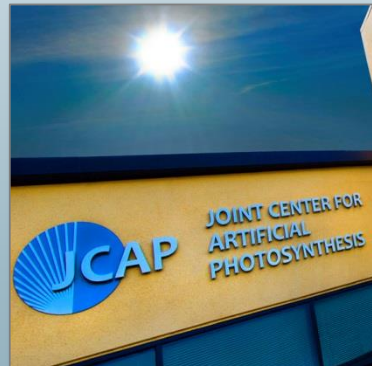
The Joint Center for Artificial Photosynthesis – At a Glance

5 Leading Research Institutions



Two Dedicated Research Laboratories

Jorgensen Laboratory

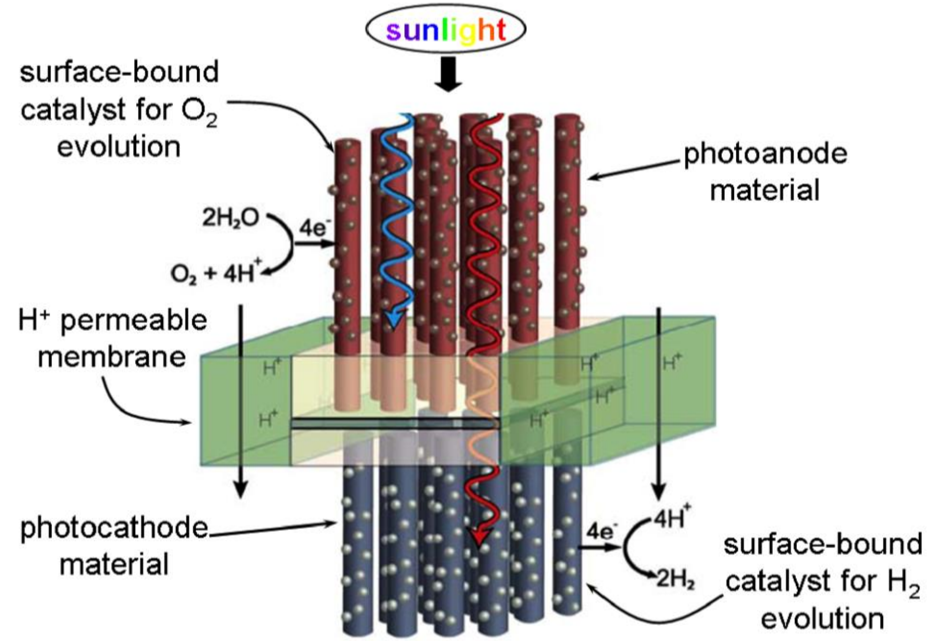
Solar-Energy Research Center

140 Scientists and Engineers

TARGET TECHNOLOGY: ANODE MATERIALS FOR TANDEM SOLAR FUELS GENERATOR

- To enhance device efficiency, an **oxygen evolution electrocatalyst** is often incorporated into the photoanode
  - For material discovery, catalyst can be screened electrochemically (no illumination)
- **Photoanodes** must be oxidatively stable in electrochemical environment
  - Band gap ≤ 2 eV is critical for efficient solar light capture

Possible solar fuel device:



$$H_2O + 4(h\upsilon) \rightarrow H_2 + 0.5\,O_2$$

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Combinatorial Materials Science, some early beginnings at LBNL

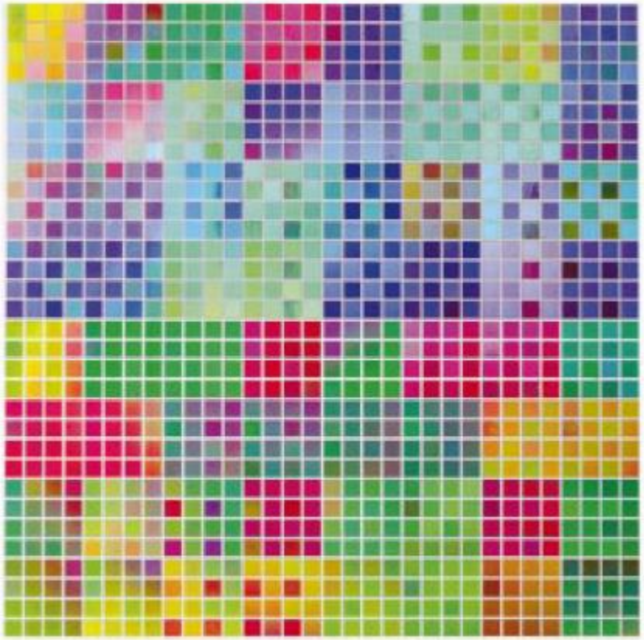
Identification of a Blue Photoluminescent Composite Material from a Combinatorial Library

Jingsong Wang, Young Yoo, Chen Gao, Ichiro Takeuchi, Xiaodong Sun, Hauyee Chang, X.-D. Xiang,* Peter G. Schultz*

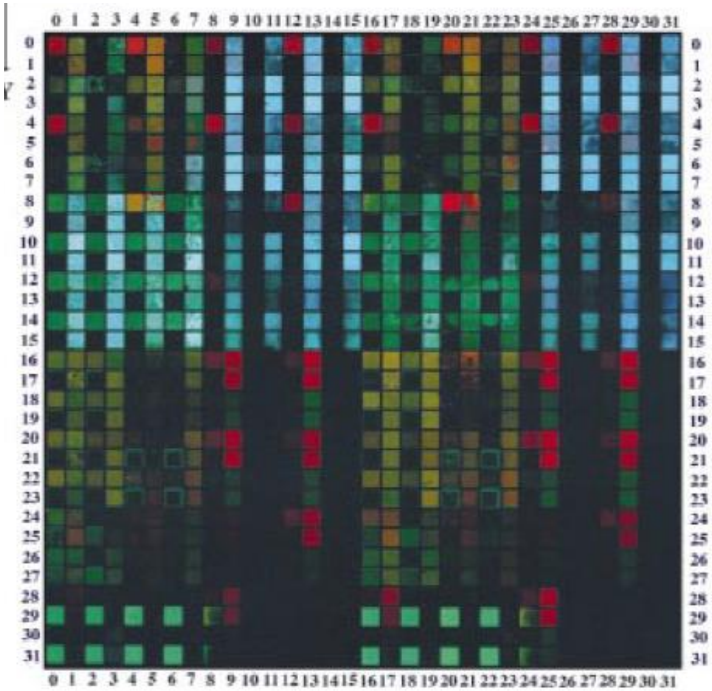
J. Wang, C. Gao, I. Takeuchi, X.-D. Xiang, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.
Y. Yoo, Department of Physics, University of California, Berkeley, CA 94720, USA.
X. Sun and H. Chang, Department of Chemistry, University of California, Berkeley, CA 94720, USA.
P. G. Schultz, Materials Sciences Division, Lawrence Berkeley National Laboratory, and Howard Hughes Medical Institute, Department of Chemistry, University of California, Berkeley, CA 94720, USA.

SCIENCE • VOL. 279 • 13 MARCH 1998 • www.sciencemag.org

White light photograph



Luminescence under UV illumination



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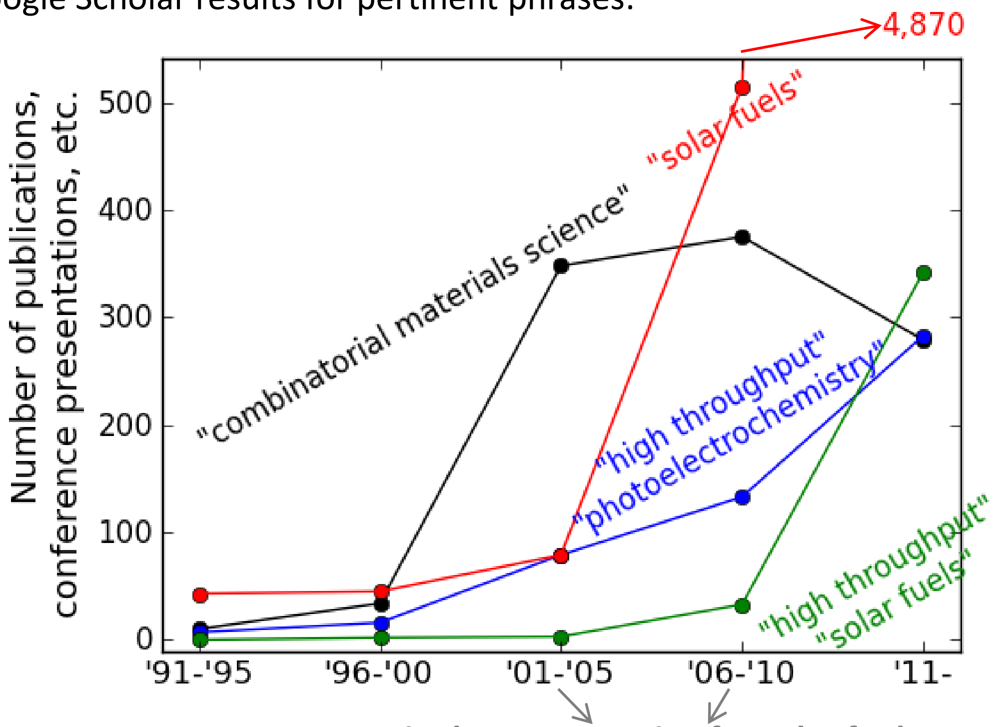
CMS and HiTp Publication Trends

Google Scholar results for pertinent phrases:



seminal papers on HiTp for solar fuels:

- **In past 25 years there have been many high throughput and combinatorial efforts**
  - **Many "lessons learned"**
  - **pre-2012: Many concepts but very little technology directly applicable to JCAP-HTE**

1. Woodhouse, M.; … Parkinson, B. A., Combinatorial approach to identification of catalysts for the photoelectrolysis of water. *Chem Mater* 2005, *17* (17), 4318-4324.
2. Jaramillo, T. F; … McFarland, E. W., Automated electrochemical synthesis and photoelectrochemical characterization of Zn1-xCoxO thin films for solar hydrogen production. *J Comb Chem* 2005, *7* (2), 264-271.
3. Jang, J. S.; … Bard, A. J., Rapid Screening of Effective Dopants for Fe2O3 Photocatalysts with Scanning Electrochemical Microscopy and Investigation of Their Photoelectrochemical Properties. *J Phys Chem C* 2009, *113* (16), 6719-6724.
4. Katz, J. E.; … Lewis, N. S., Combinatorial synthesis and high-throughput photopotential and photocurrent screening of mixed-metal oxides for photoelectrochemical water splitting. *Energ Environ Sci* 2009, *2* (1), 103-112.

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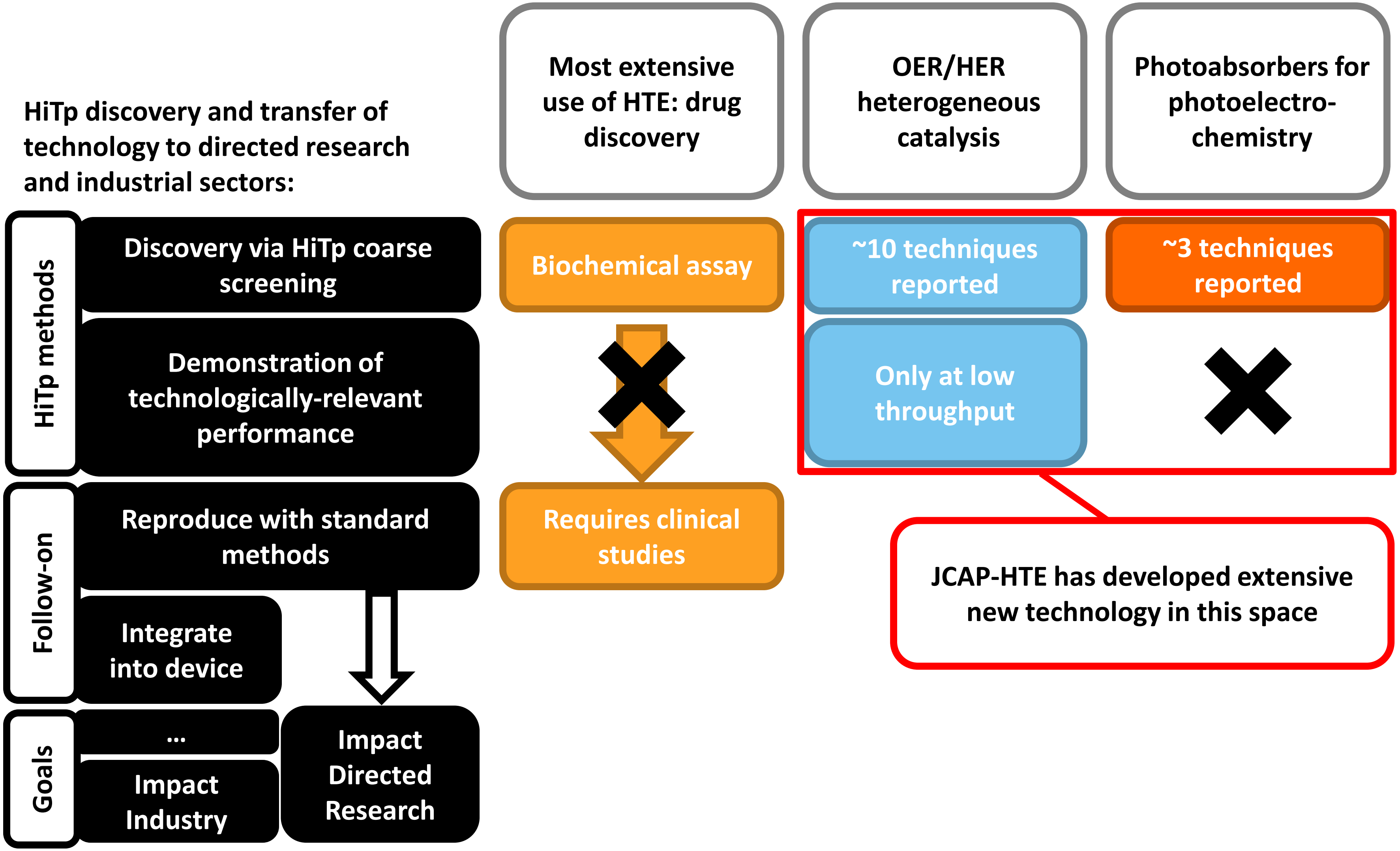
Historical starting points for JCAP HTE screening

HiTp discovery and transfer of technology to directed research and industrial sectors:



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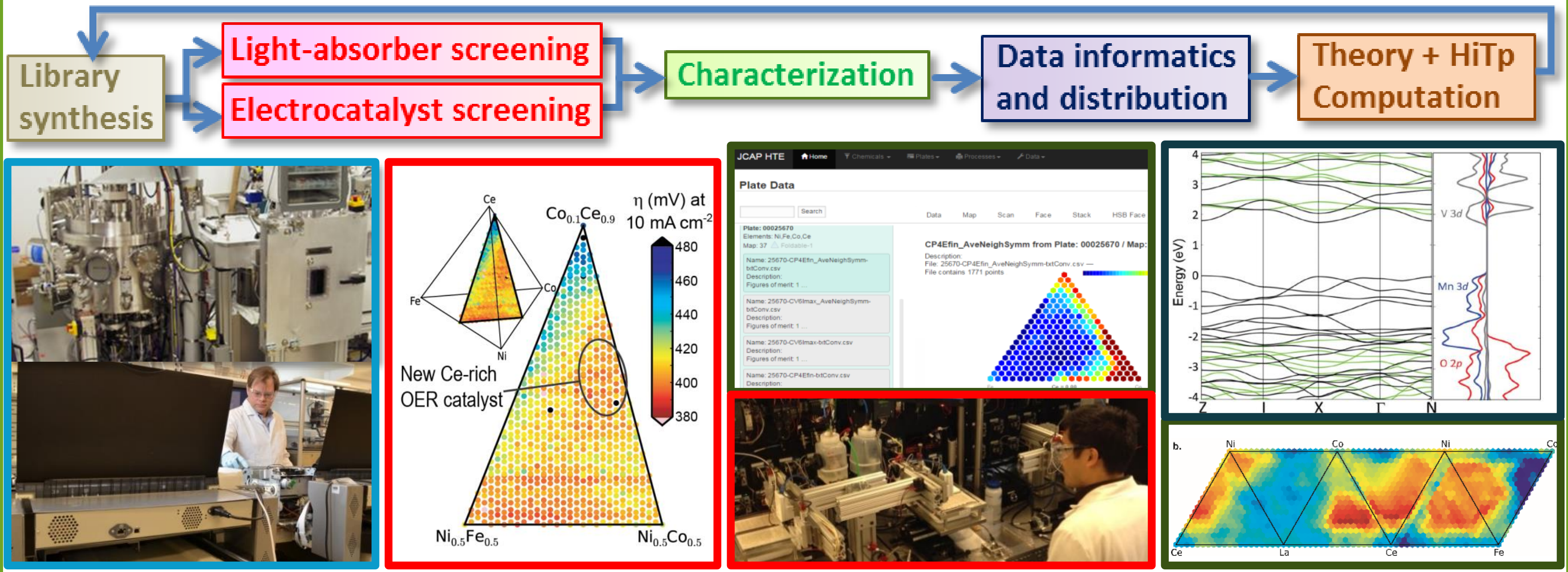
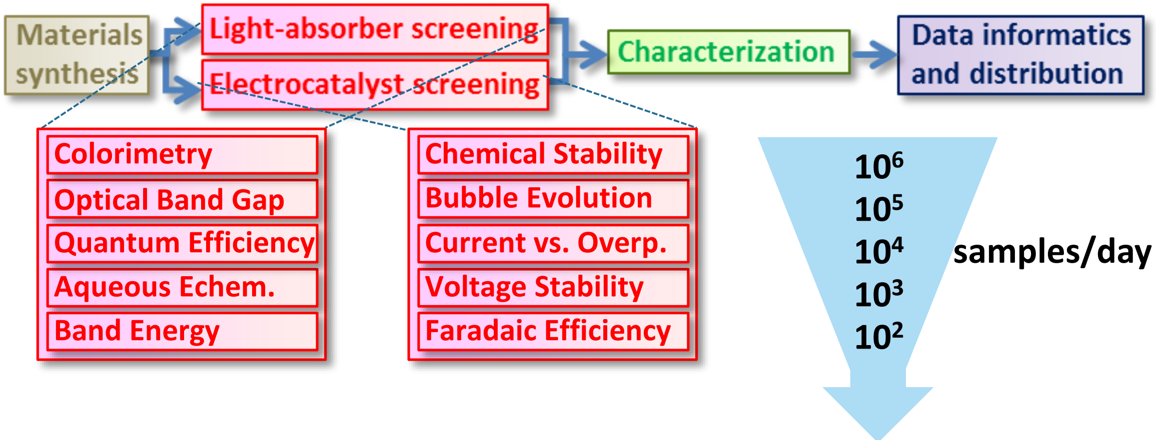
HiTp Pipeline: A Network of Instrumentation and Computational Capabilities

- Design of a HTE pipeline must be
  - specific to the target technology
  - integrated into the broader research community
  - Balance throughput with data quality



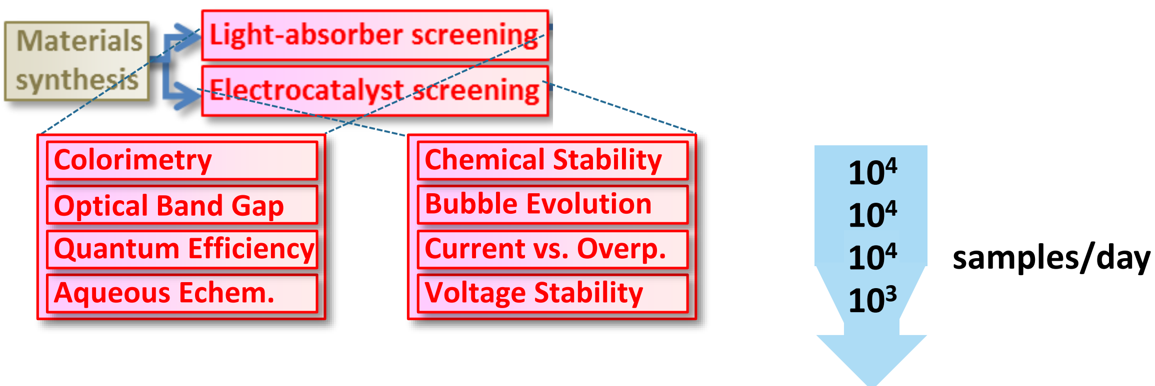
Tiered screening and HTE pipeline throughput

Ultimate solar fuels HTE pipeline

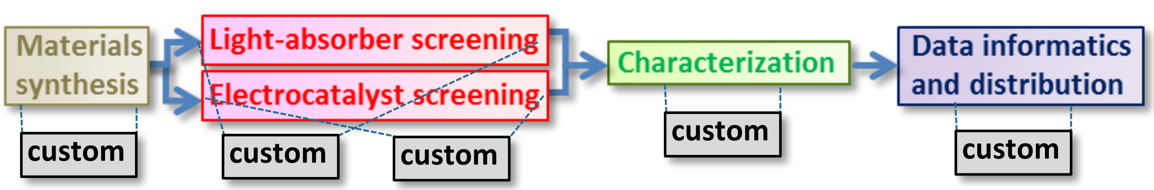


- **3 example implementations of a high throughput experimental pipeline**

Pipeline v1



HTE-CMS (Combinatorial Material Science)



Limited by custom data handling, ~10^3 samples/month

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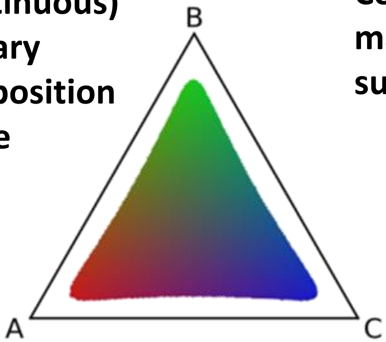
Combinatorial and High Throughput Material Science

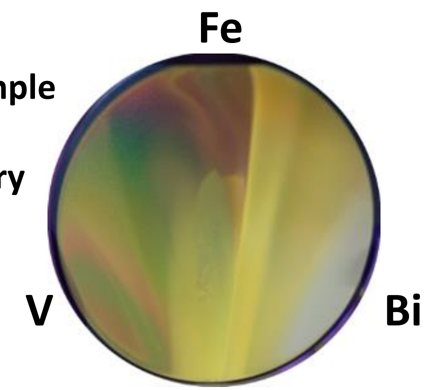
- **Measurement of material properties as a function of composition and/or processing**
  - **JCAP-HTE employs 2 complementary deposition methods and has developed several processing methods**
    - PVD synthesis of continuous composition libraries
    - Inkjet printing of elemental precursors and post-calcinations

(continuous) Ternary composition space

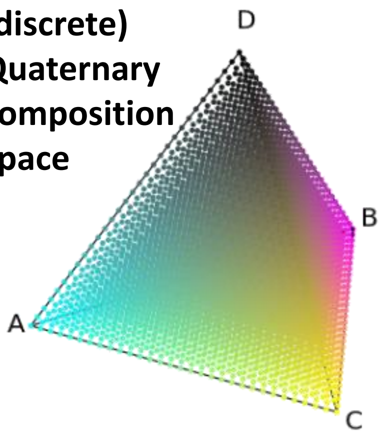


Composition map onto substrate

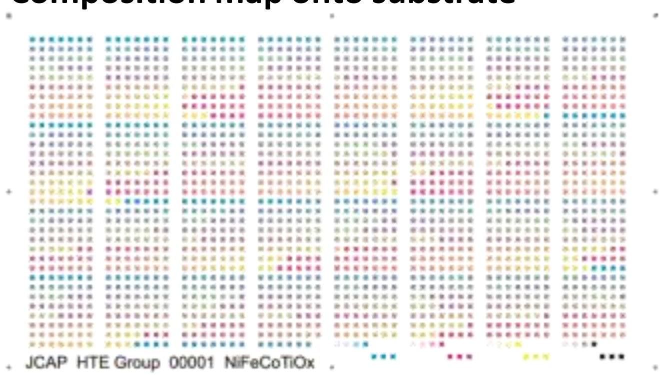
Example PVD library



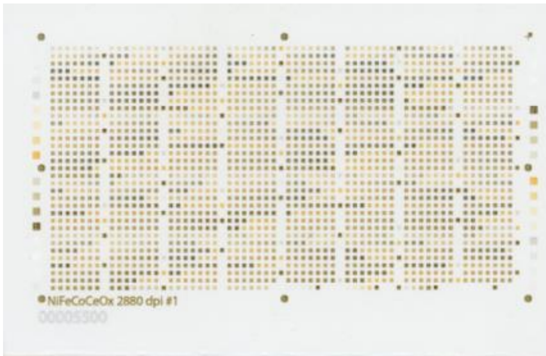
(discrete) Quaternary composition space



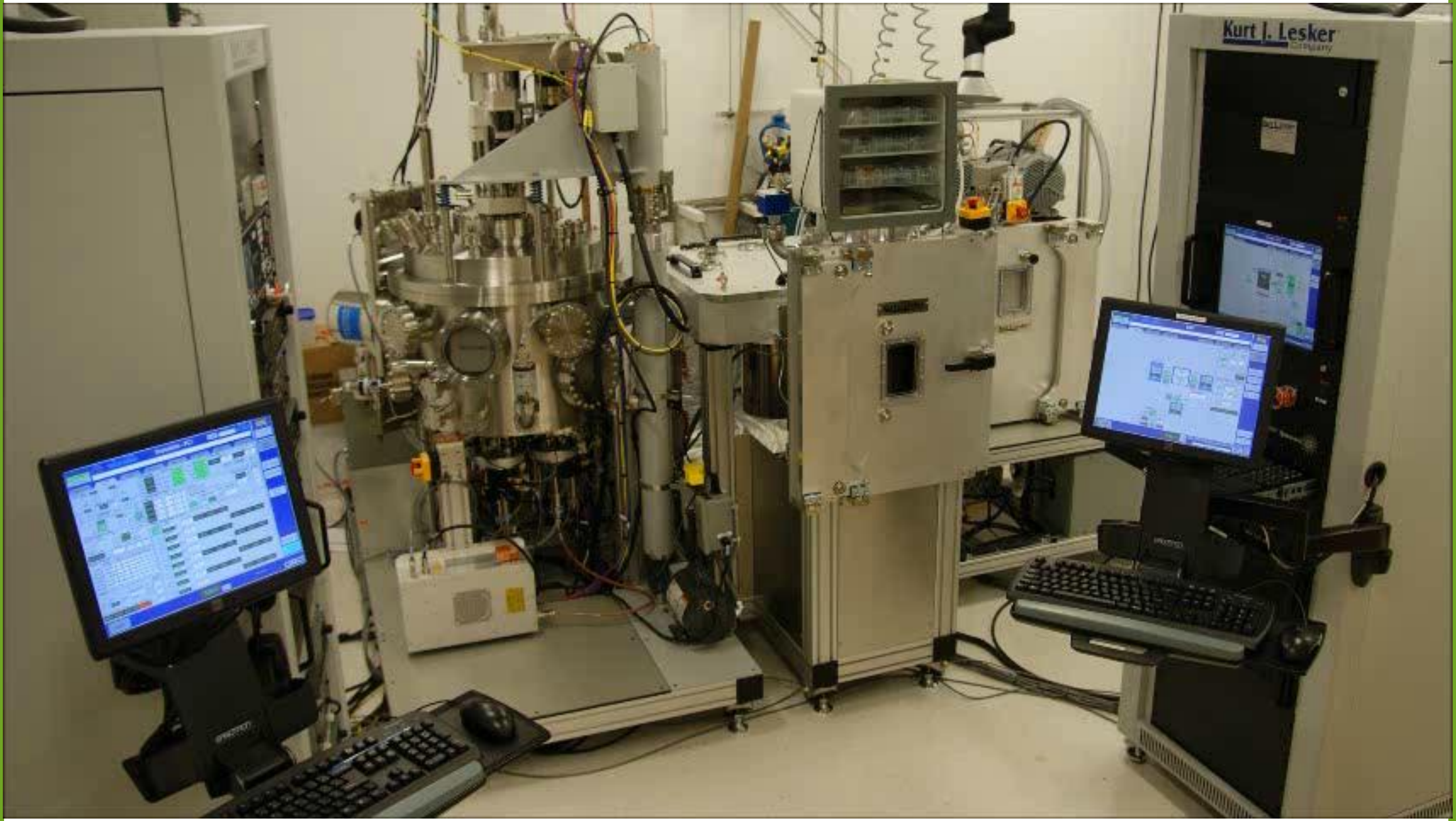
Composition map onto substrate



Example inkjet printed library



LIBRARY SYNTHESIS OVERVIEW



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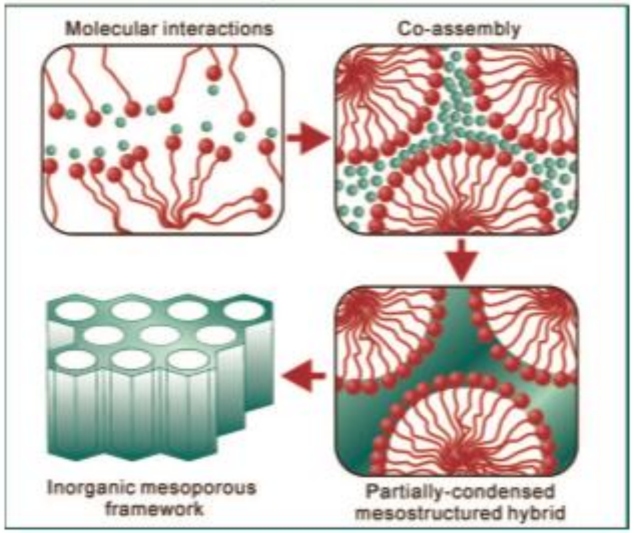
Ethanol-Based Inks—A Key Enabling Technology

Sophisticated Materials Synthesis Platform



Oxide Precursor Ink Formulations Contain:

- Metal precursor: nitrate (NO_3), halide (Cl), or alkoxide (-OR)
- Complexing (stabilizing) agent: acetic acid
- Strong Acid: HNO_3, HCl, etc.
- Multifunctional structure directing agent (SDA) from the Pluronic or Brij family of triblock (PEO-PPO-PEO) copolymers: F127, P123, etc.

Performance:

- SDA modifies viscosity and surface tension to match the printer requirements.
- SDA modifies wetting and viscosity to maintain discreet 1 mm^2 composition spots.
- Stabile inks for 10s to 100s of hours.
- SDA co-assembles with the metal oxide precursor to produce – in some cases—mesoporous, nanostructured materials
- Promotes mixing of metals at the atomic level.

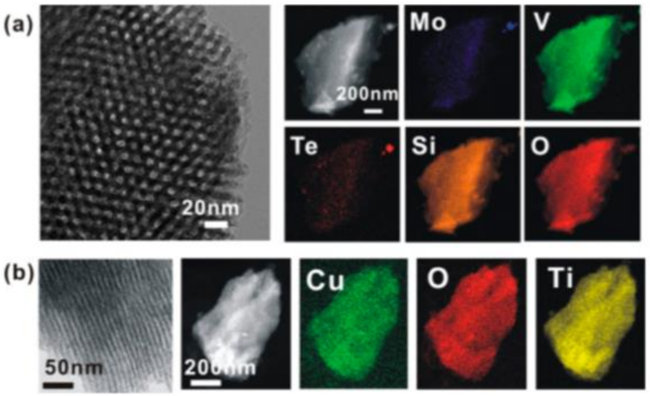
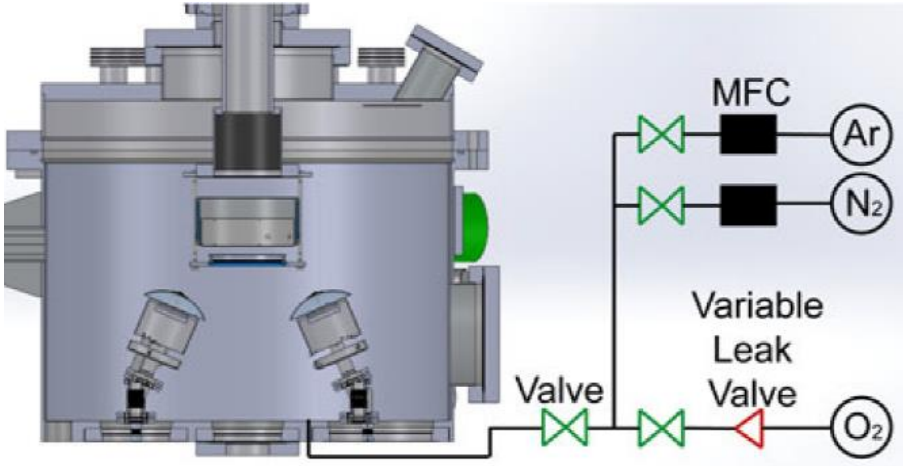


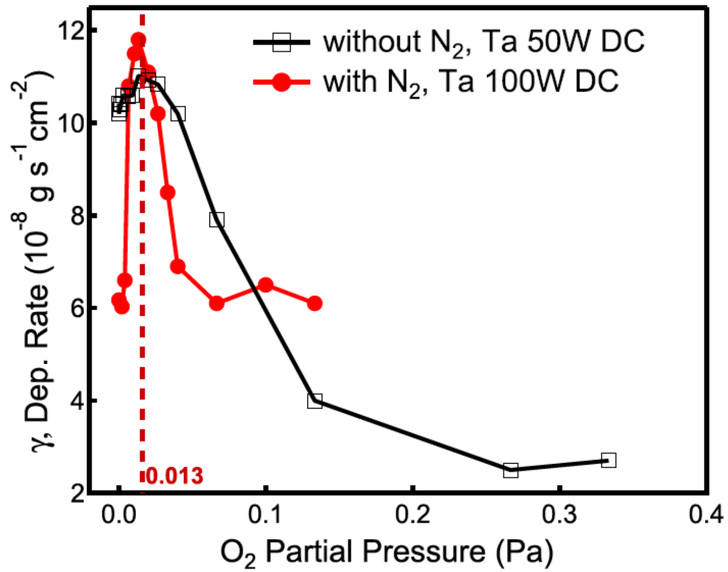
Figure 2. Transmission electron microscopy (TEM) images and dispersive X-ray spectroscopy (EDX) element mapping of mesostructured (a) $Mo_{0.05}V_{0.01}Te_{0.01}Si_{1.0}O_w$ and (b) $Cu_{0.004}TiO_w$, revealing a homogeneous distribution of each component in the printed mesoporous materials.

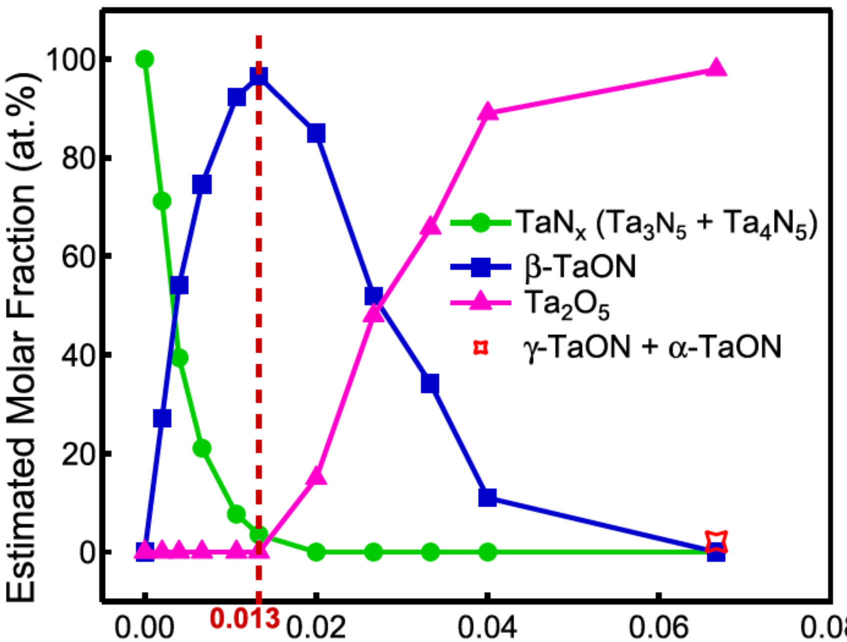
Sophisticated ink formulations required to produce defined library composition spots with atomic level mixing

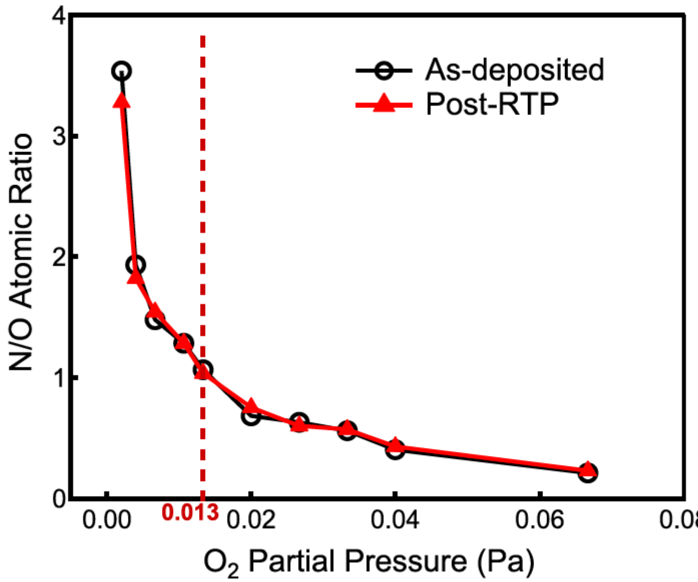
S. W. BOETTCHER, J. FAN, C.-K. TSUNG, Q. SHI, G. D. STUCKY* Acc. Chem. Res. 2007, 40, 784–792

Development of PVD depositiion of Oxynitrides









Zhou, L., Suram, S. K., Becerra-stasiewicz, N., Mitrovic, S., & Kan, K. (2015). Combining reactive sputtering and rapid thermal processing for synthesis and discovery of metal oxynitrides. J. Mater. Res., http://dx.doi.org/10.1557/jmr.2015.140.

EXAMPLE TRADITIONAL ELECTROCATALYST EVALUATION

- **Prepare catalyst on end cap of a cylinder**
- **Prepare 100 mL of electrolyte solution**
- **Calibrate reference electrode**
- **Assemble 3-electrode cell**
- **Spin catalyst at 1000 rpm to mitigate diffusion limitations**
- **Perform various electrochemical experiments (CP, CA, CV), particularly ~200 s / cycle CV**
- **Discard solution**

>90% of time on experiment preparation. Need comparable data with automated, rapid cell preparation.

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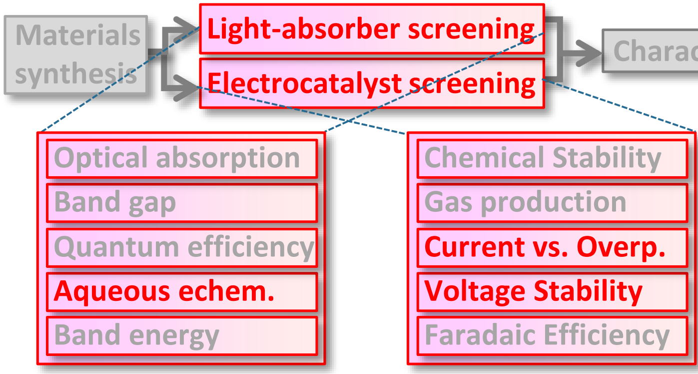
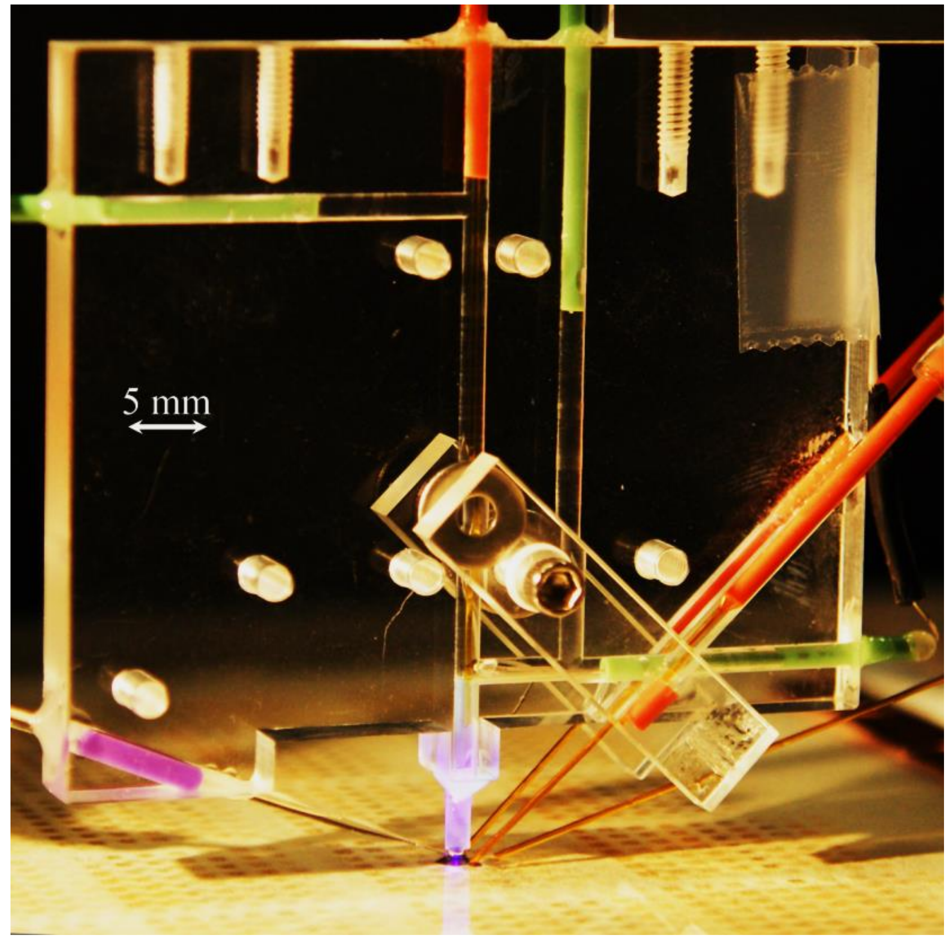
SCANNING DROP CELL



- Establishes 3 electrode cell for each sample
- Gasket-free for rapid, on-demand rastering
- Low uncompensated resistance for rapid scanning and data interpretation
- Fiber-coupled for photoelectrochemistry
- Flow cell eliminates cross contamination
- Demonstrated 1V CV at 4s per sample, **~50x faster than any previous scanning instrument**
- Complete software automation and real-time analysis



J. M. Gregoire, C. Xiang, X. Liu, M. Marcin, J. Jin, Rev. Sci. Instrum. 84, 024102 (2013)

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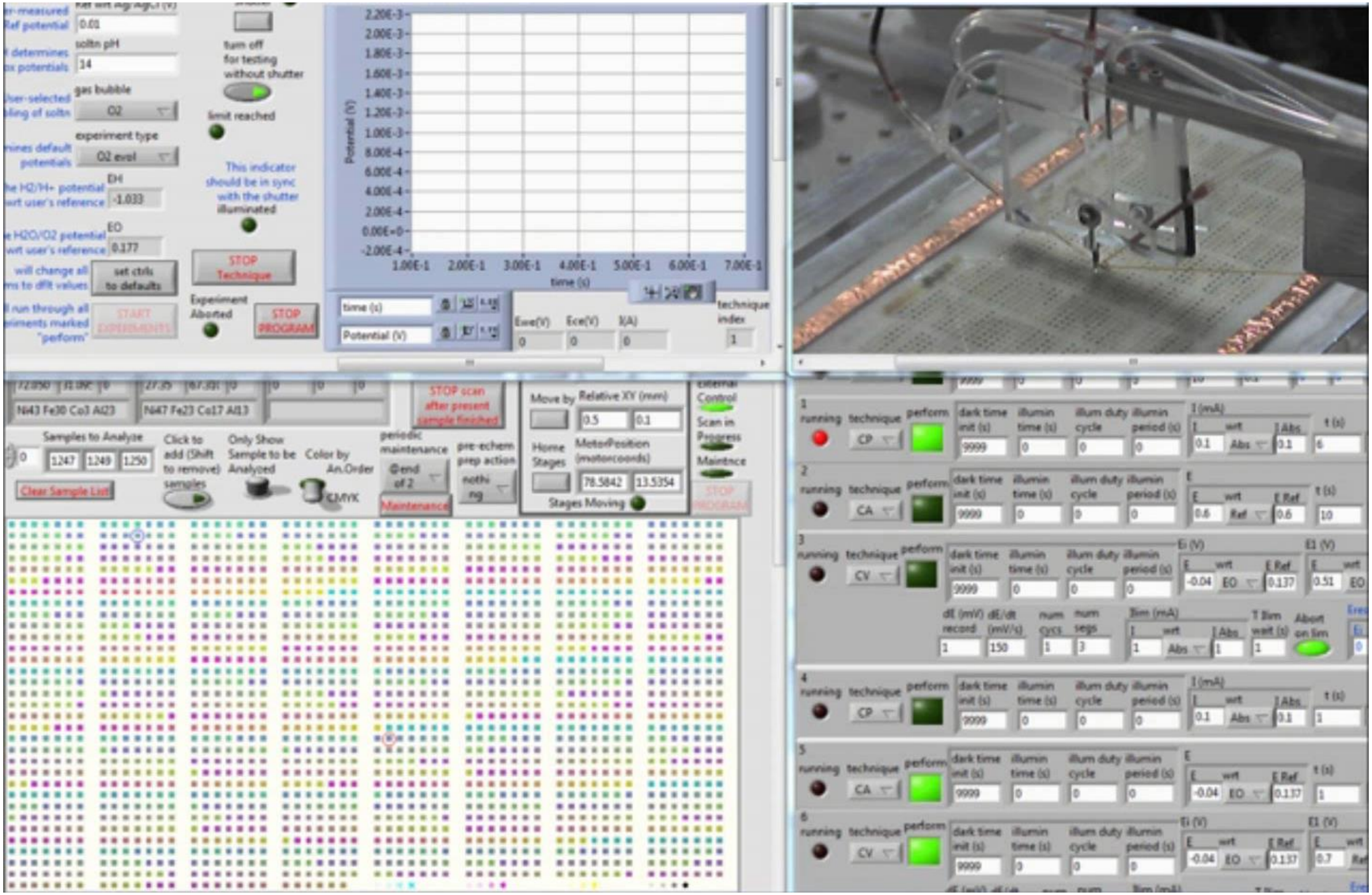
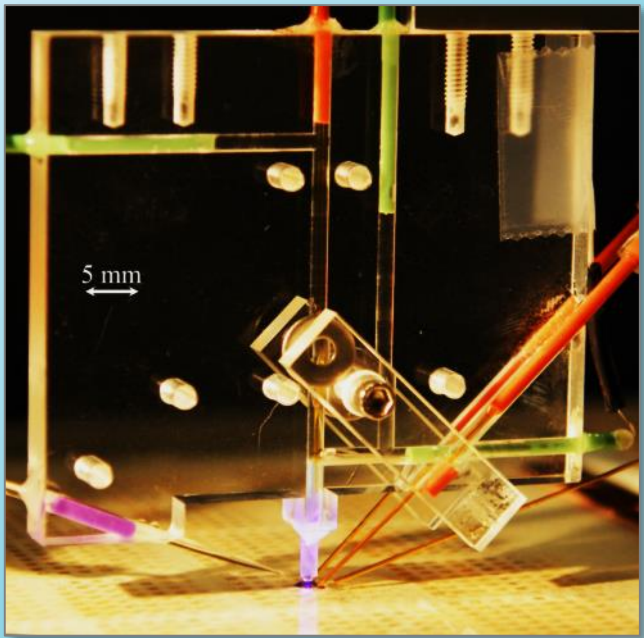
Example Automated HiTp Screening

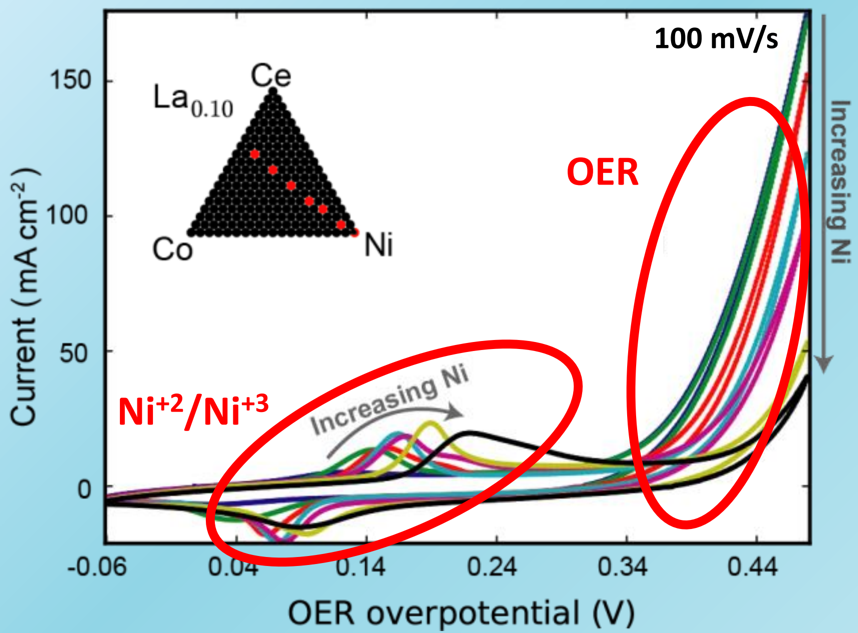


High-Throughput Electrochemical Screening

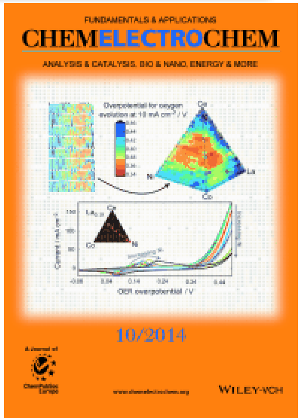
Scanning Droplet Cell (SDC) *



Current-voltage curve +



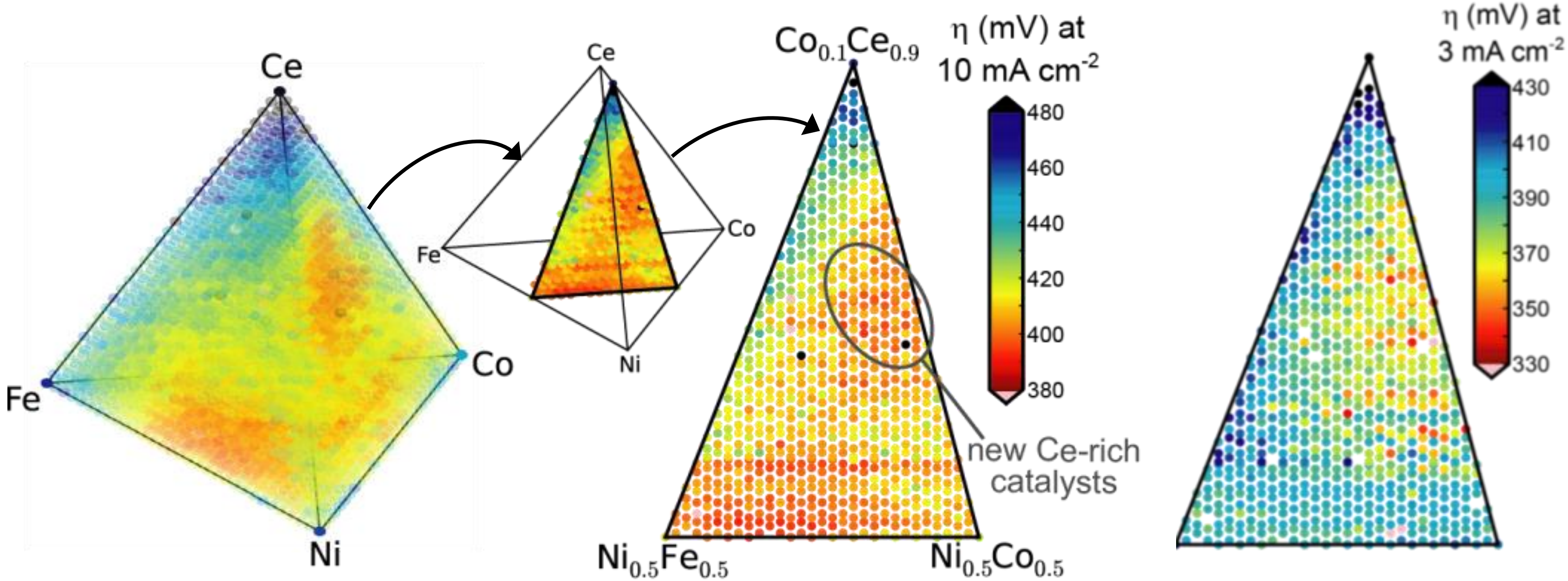
- **3-electrode cell**
- **Rapid solution flow**
- **Low uncompensated resistance**

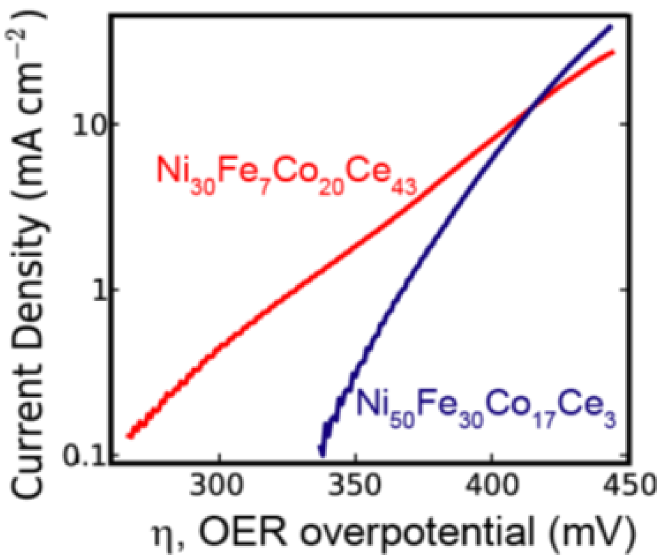


* J. M. Gregoire, C. Xiang, X. Liu, M. Marcin, and J. Jin *Rev. Sci. Inst.* **2013**, *84*, 024102. (DOI: 10.1063/1.4790419)

+ Haber, J. A., D. Guevarra, et al. *ChemElectroChem* **2014** (DOI: 10.1002/celc.201402306).

Ni-Fe-Co-Ce-O_x OER catalyst discovered





Spot	Target Composition (at%)	EDX Composition (at%)
1	$Fe_{0.03}Co_{0.30}Ce_{0.67}$	$Fe_{0.06}Co_{0.33}Ce_{0.64}$
2	$Ni_{0.03}Fe_{0.17}Co_{0.13}Ce_{0.67}$	$Ni_{0.02}Fe_{0.18}Co_{0.14}Ce_{0.67}$
3	$Ni_{0.20}Fe_{0.03}Co_{0.33}Ce_{0.43}$	$Ni_{0.18}Fe_{0.05}Co_{0.34}Ce_{0.43}$
4	$Ni_{0.23}Fe_{0.03}Co_{0.23}Ce_{0.50}$	$Ni_{0.25}Fe_{0.06}Co_{0.21}Ce_{0.41}$
5	$Ni_{0.23}Fe_{0.07}Co_{0.27}Ce_{0.43}$	$Ni_{0.24}Fe_{0.10}Co_{0.26}Ce_{0.40}$
6	$Ni_{0.27}Fe_{0.07}Co_{0.20}Ce_{0.47}$	$Ni_{0.33}Fe_{0.05}Co_{0.20}Ce_{0.41}$
7	$Ni_{0.30}Co_{0.27}Ce_{0.43}$	$Ni_{0.34}Co_{0.28}Ce_{0.38}$
8	$Ni_{0.33}Co_{0.27}Ce_{0.40}$	$Ni_{0.34}Co_{0.29}Ce_{0.35}$
9	$Ni_{0.33}Fe_{0.07}Co_{0.20}Ce_{0.40}$	$Ni_{0.34}Fe_{0.07}Co_{0.23}Ce_{0.35}$

OER catalysts discovered in new, unpredicted composition region with ~50% Ce

J.A. Haber, Y. Cai, S. Jung, C. Xiang, S. Mitrovic, J. Jin, A.T. Bell and J.M. Gregoire, *Energy Environ. Sci.* 7, 682 (2014)

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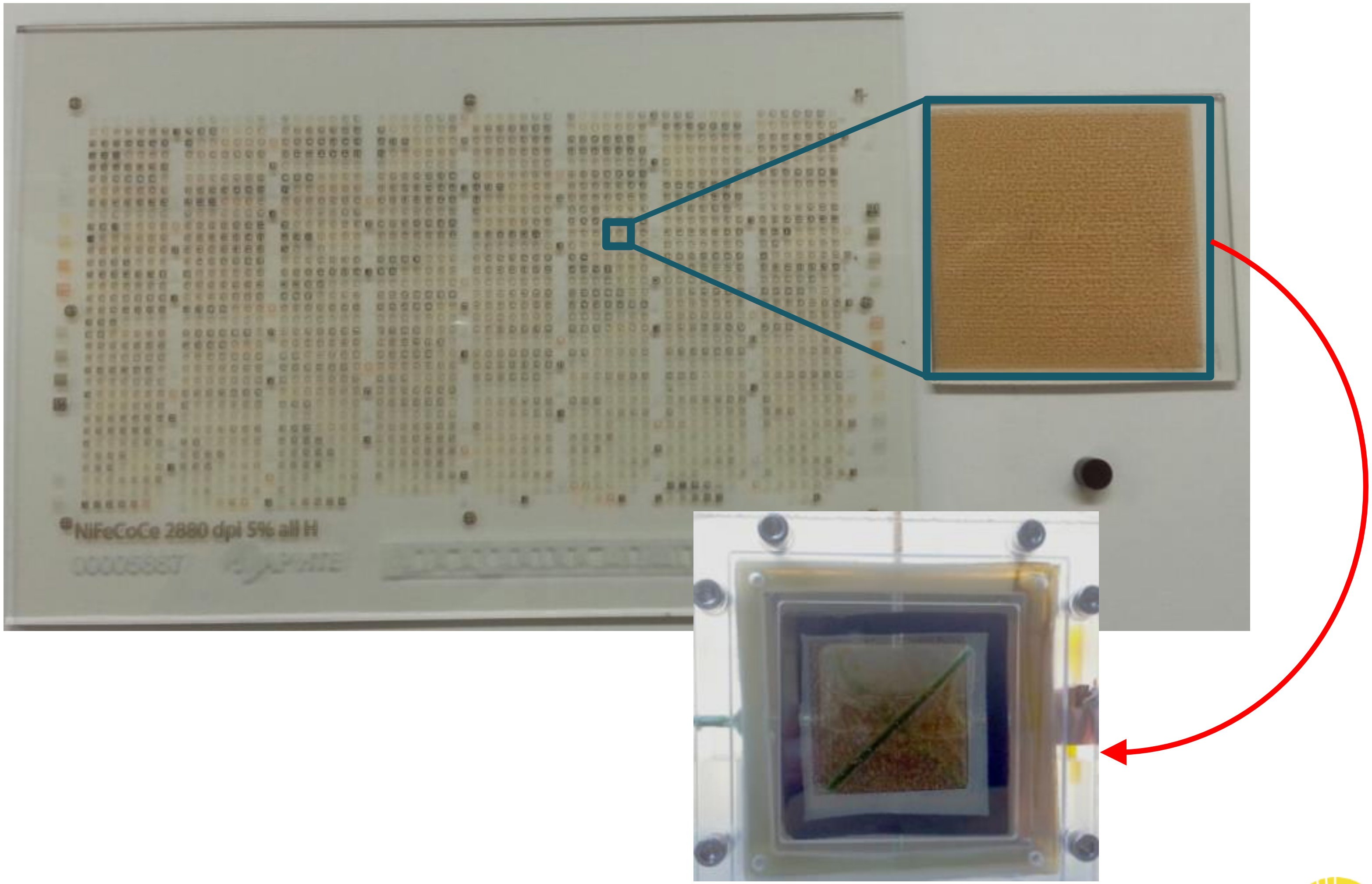
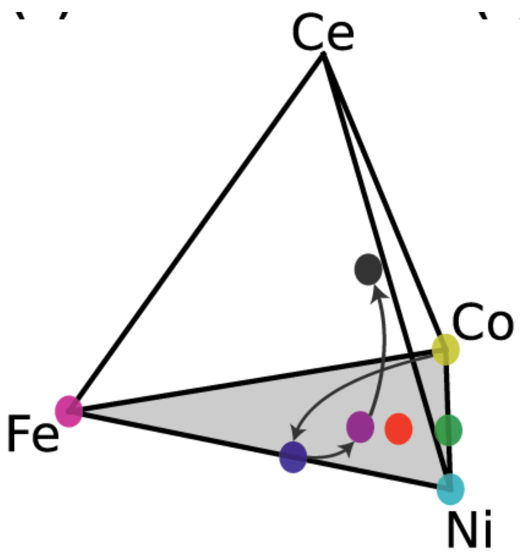
Transition of High-throughput Materials to Benchmarking and Prototyping

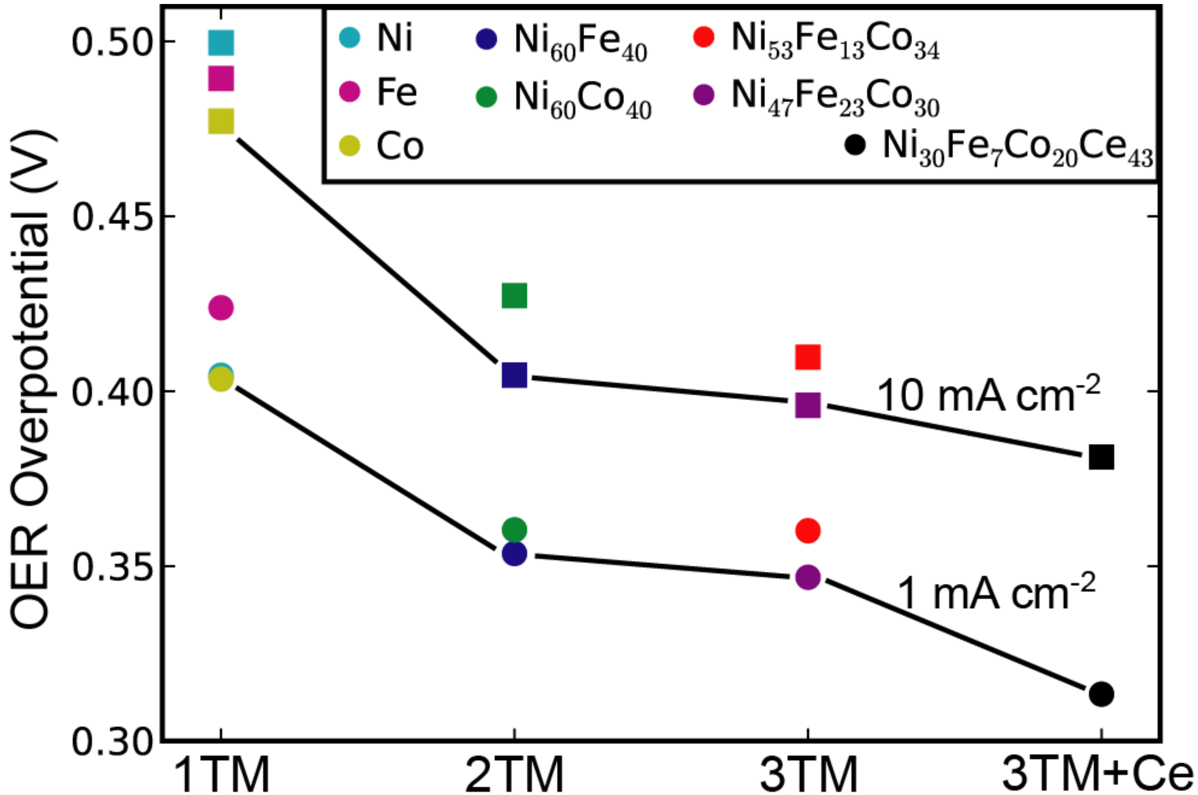
Ink-jet Printing enables rapid translation to alternate substrates



Prototyping Testbed electrolyzer

The Uniqueness of a Quinary Oxide





- Primary strategy for decades has been mixing 2 TMs
- Adding a 3rd TM exhibits diminishing returns
- Adding ~50% Ce provides great improvement even though pure CeO_x is poor catalyst

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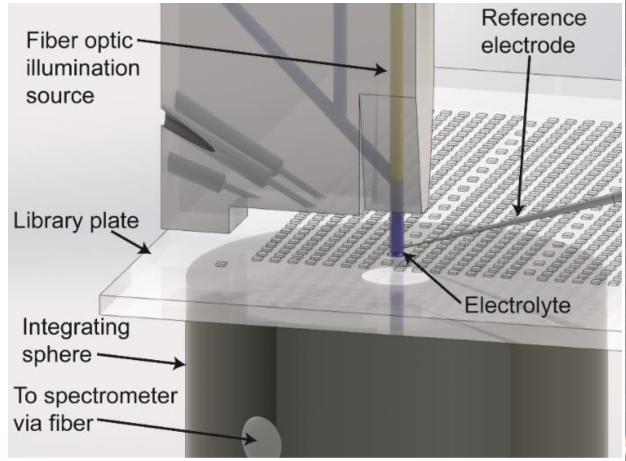
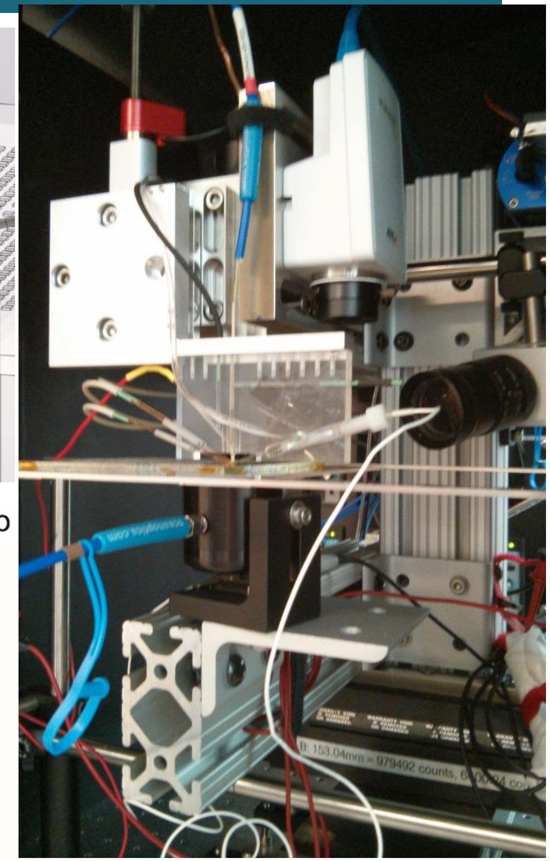
OER Catalyst Transparency Under Operation

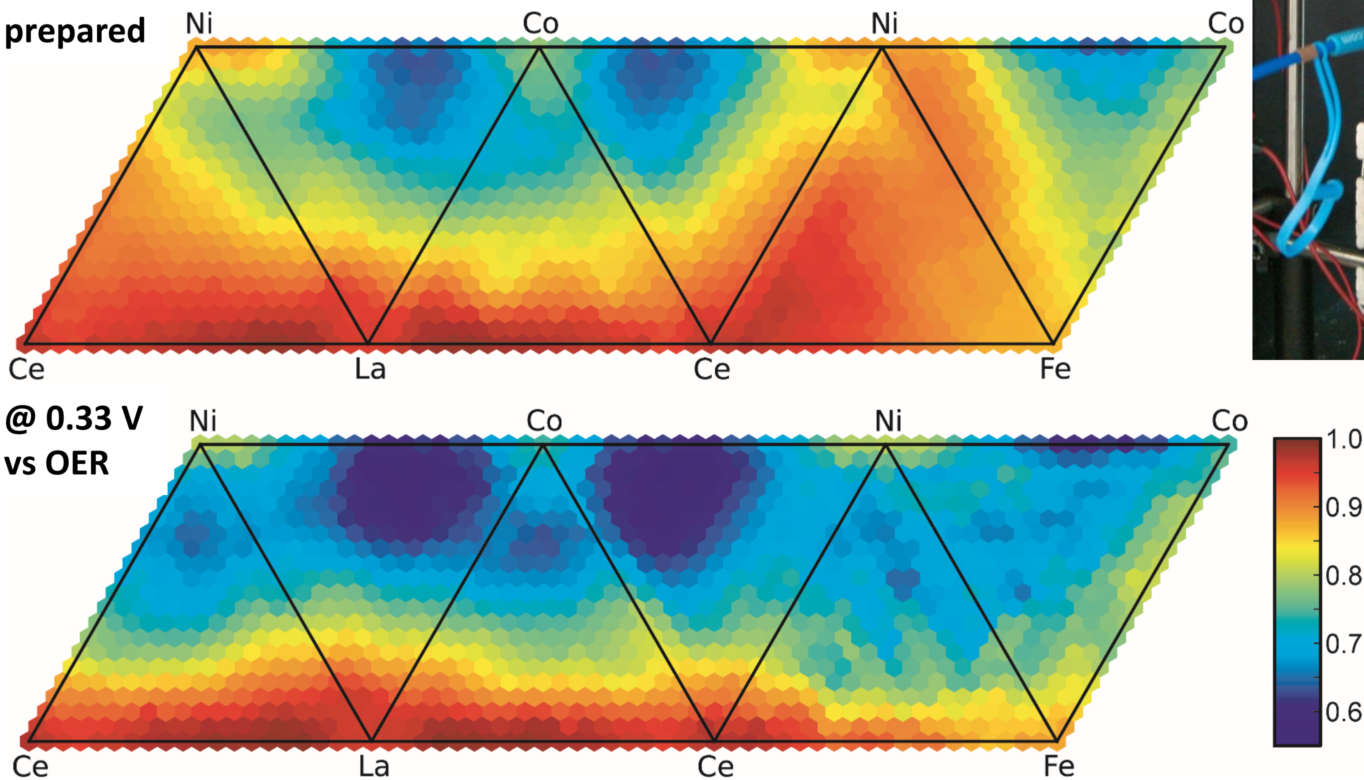
Most OER catalysts are more oxidized under operation than in ambient, requiring *in situ* optical characterization.





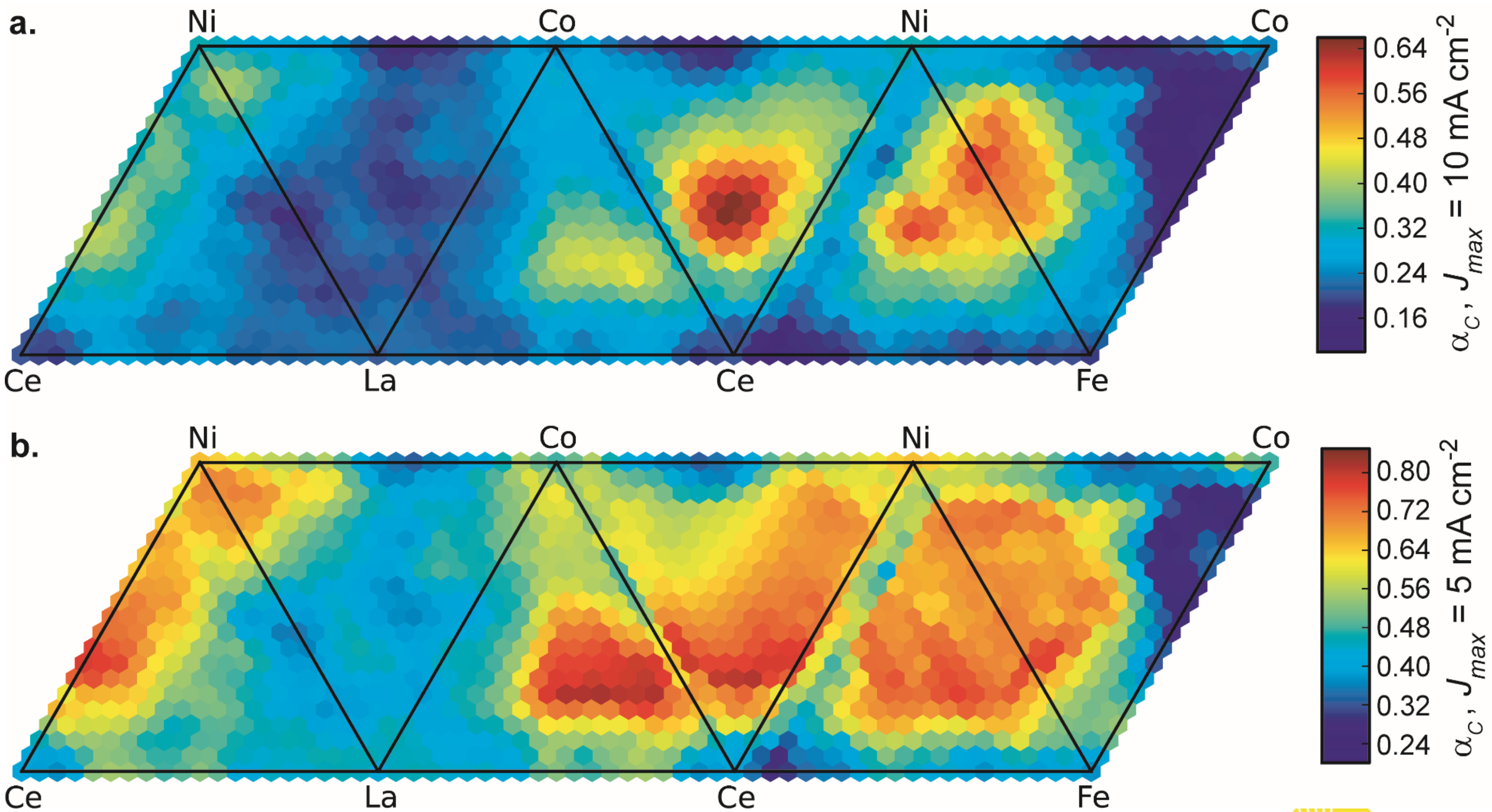
As-prepared

@ 0.33 V vs OER

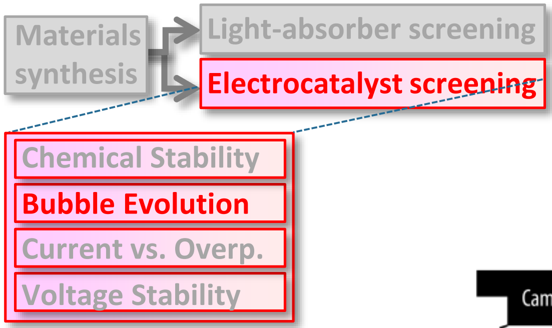


Ave. Transmission of AM 1.5

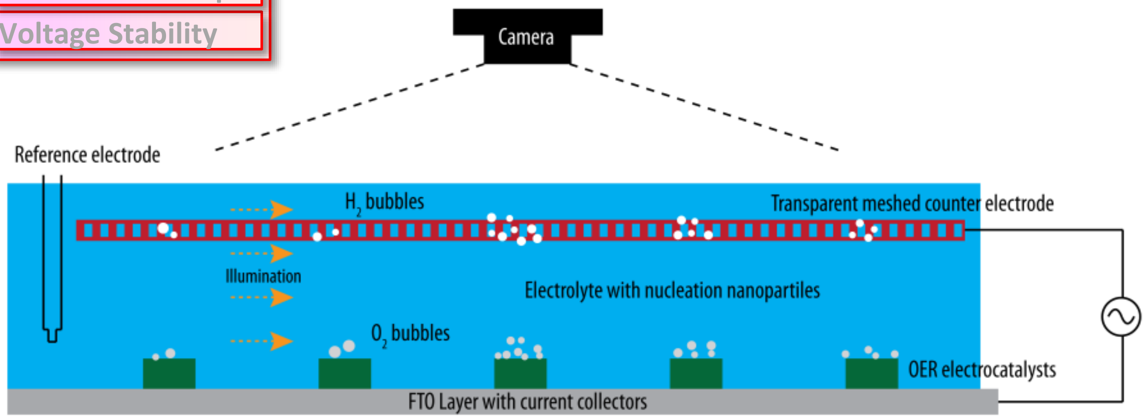
Ce-containing catalysts are optimal, and optimal composition depends on catalytic requirements



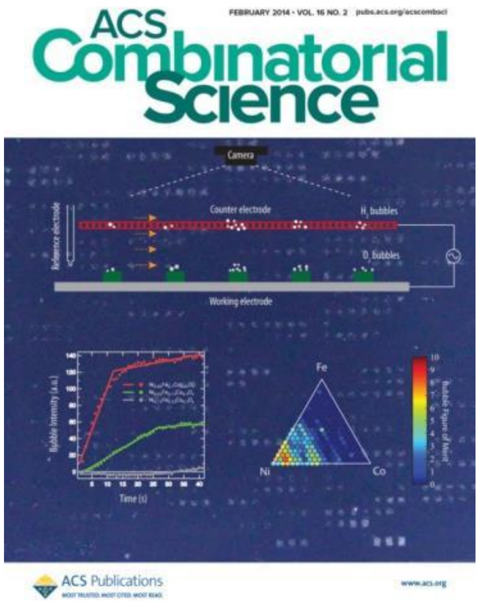
Parallel Catalyst Screen: Bubble Imaging



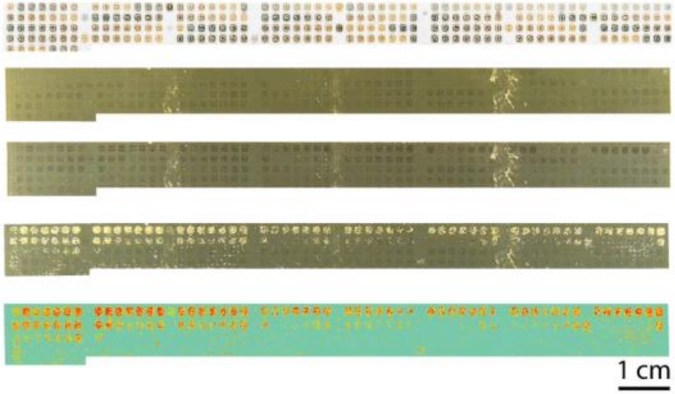
- Parallel imaging of evolved gas bubbles for HER and OER catalysts
- Independent of solution pH

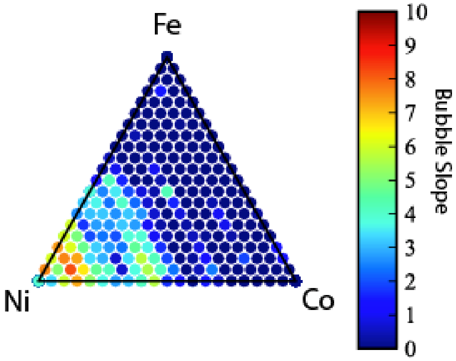


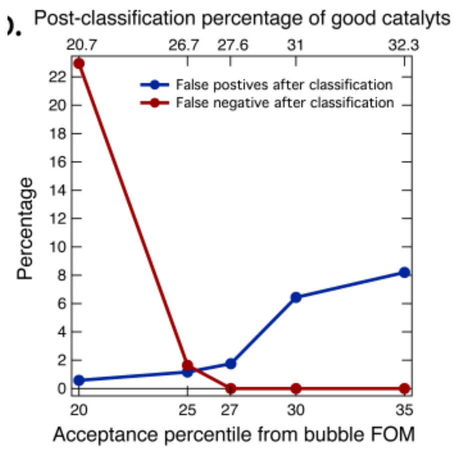
Selected as ACS Combi cover



Automated image processing



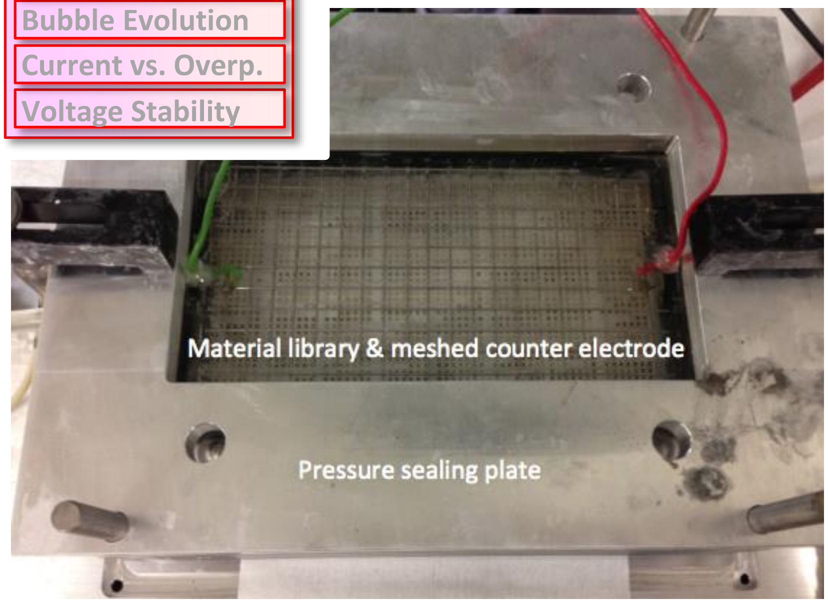


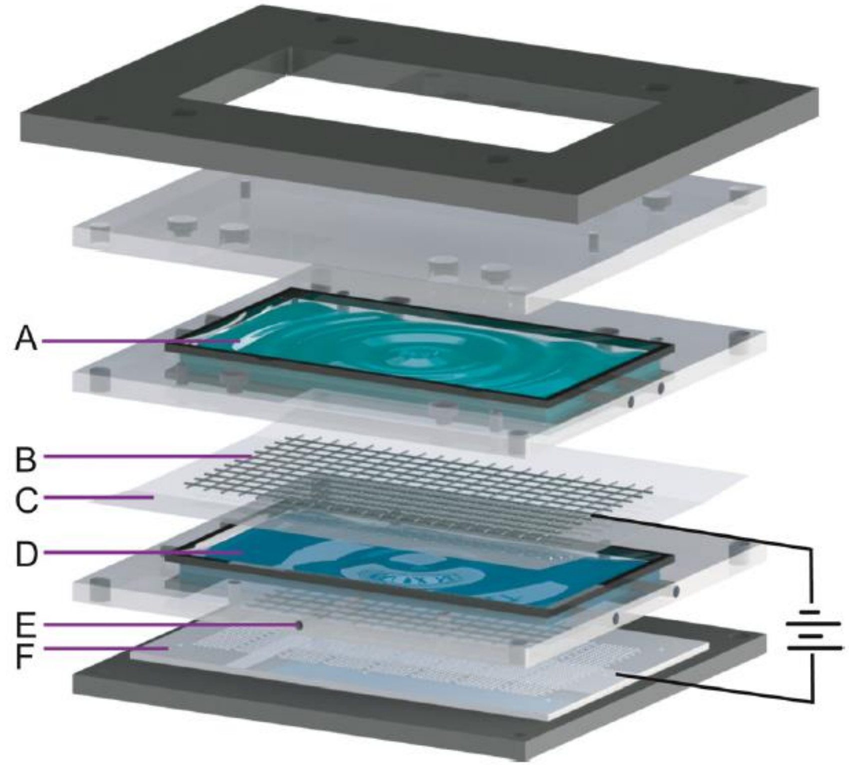


PARALLEL ELECTROCATALYST SCREEN: ACIDIC ELECTROCHEMICAL STABILITY

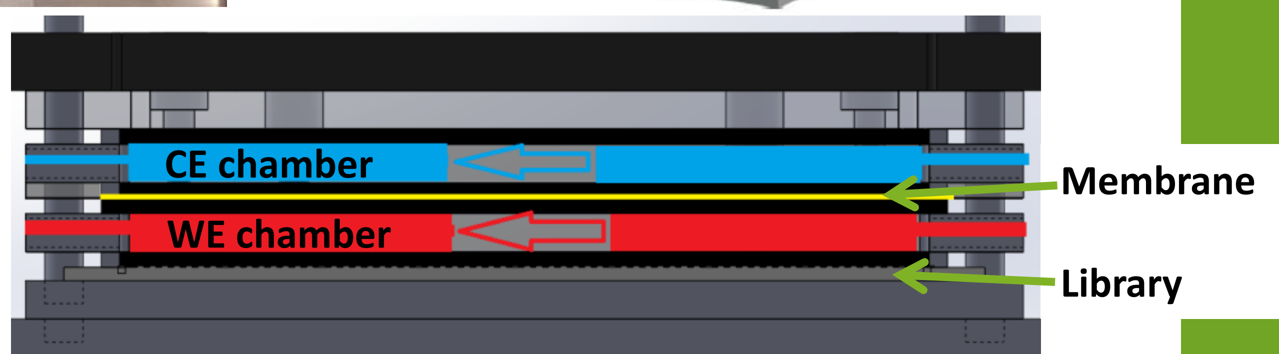
Materials synthesis → Light-absorber screening / Electrocatalyst screening

- Chemical Stability
- Bubble Evolution
- Current vs. Overp.
- Voltage Stability





- Membrane-separated chambers prevent counter electrode contamination via electroplating
- Flowing solution purges dissolved ions



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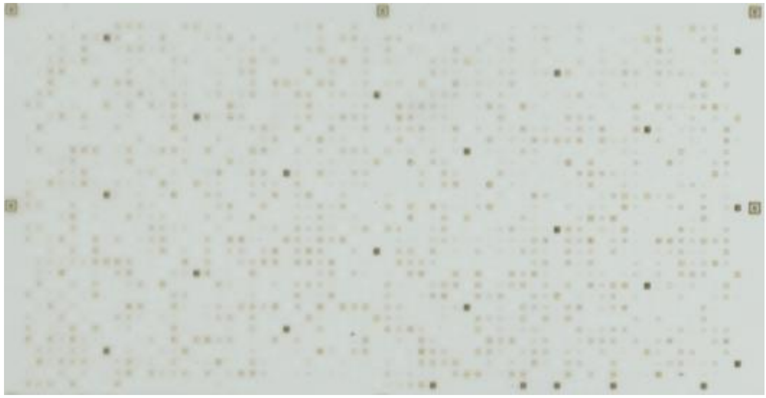
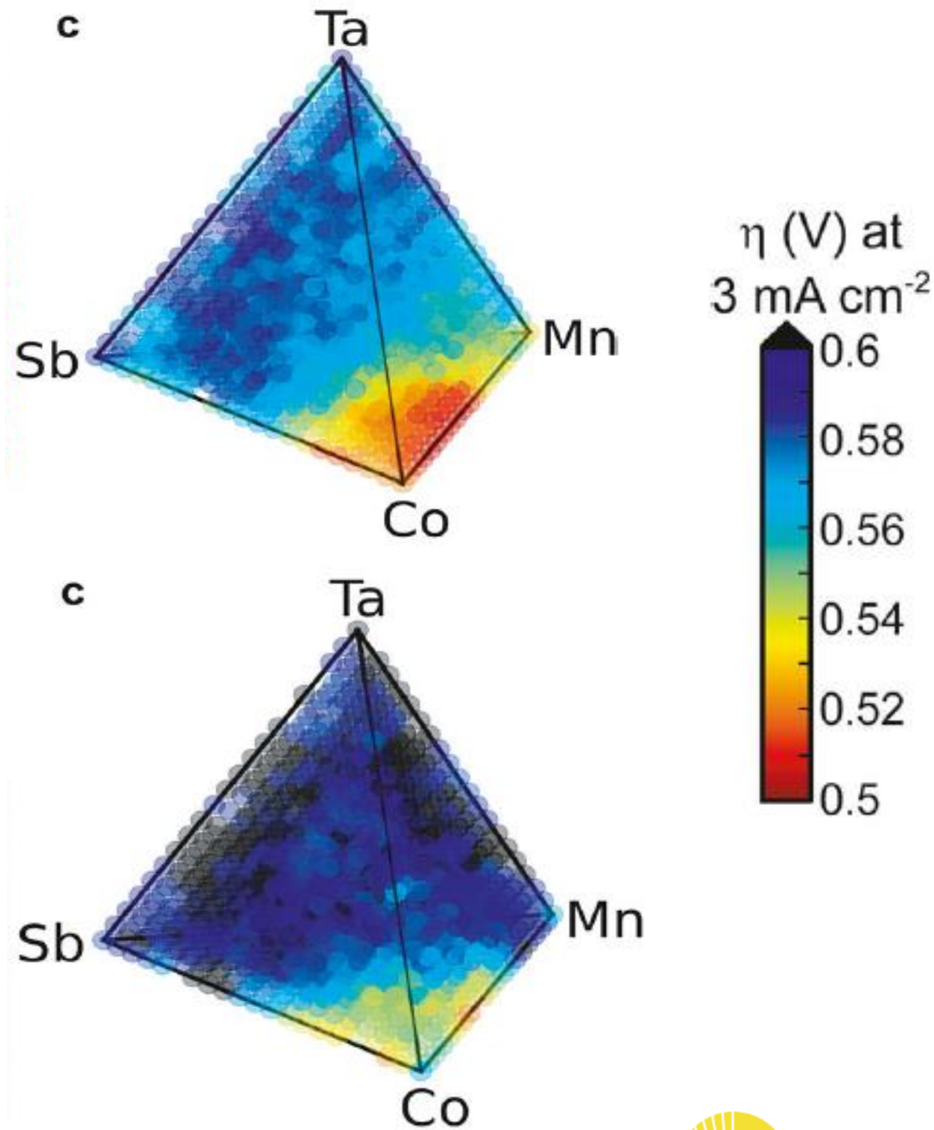
Discovery of pH 0 OER catalyst

As-prepared



After 2 hr operation at pH 0



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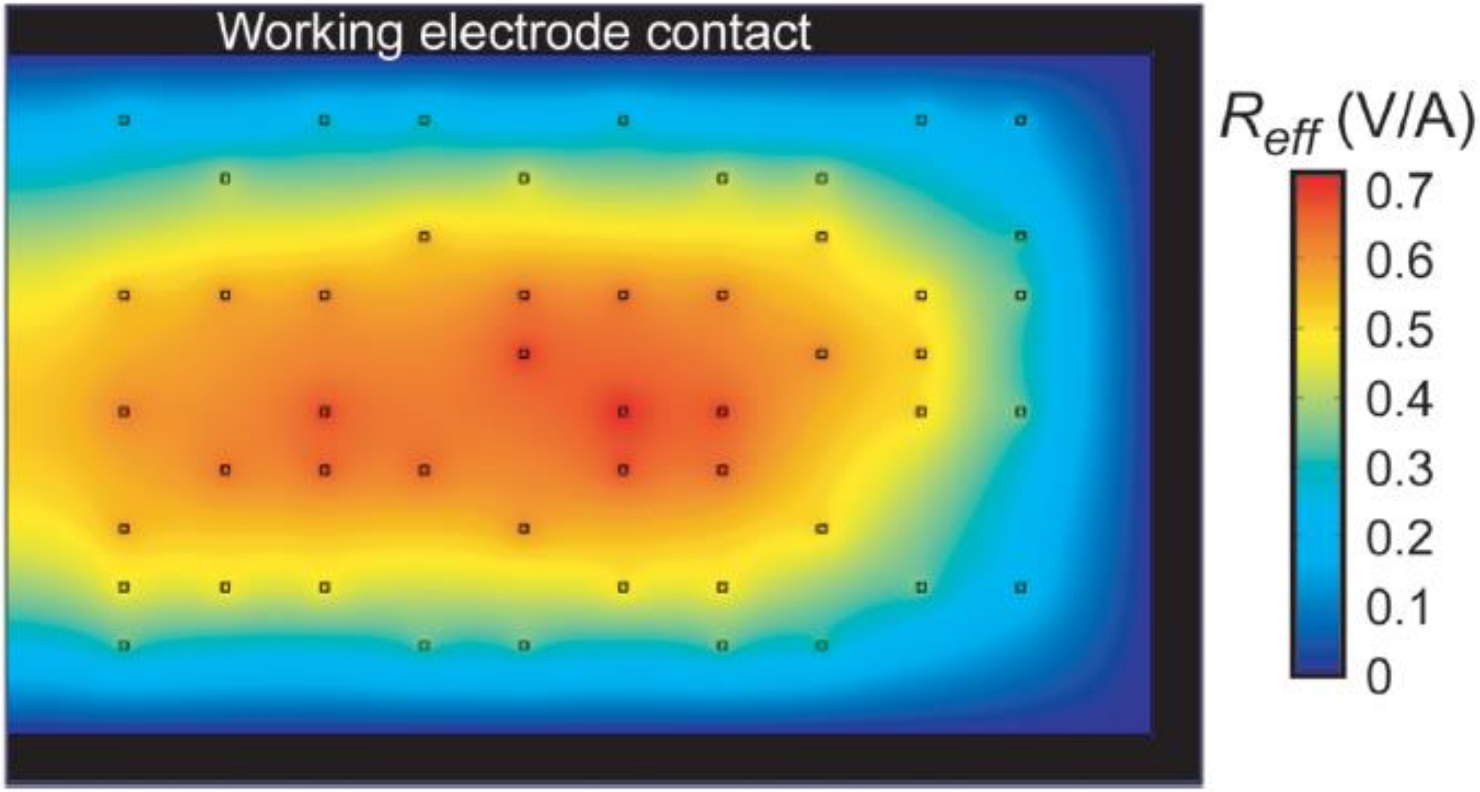
Simulation of resistive losses

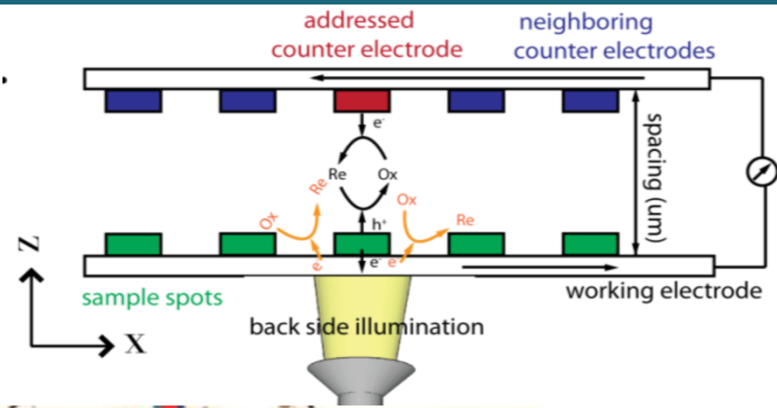
- Assume total measured current enters sheet conductor from ~50 random samples and passes through sheet conductor to perimeter contact
- For 7 Ohm/square sheet resistor, effective resistance distribution over 150 x 100 mmplate looks like:

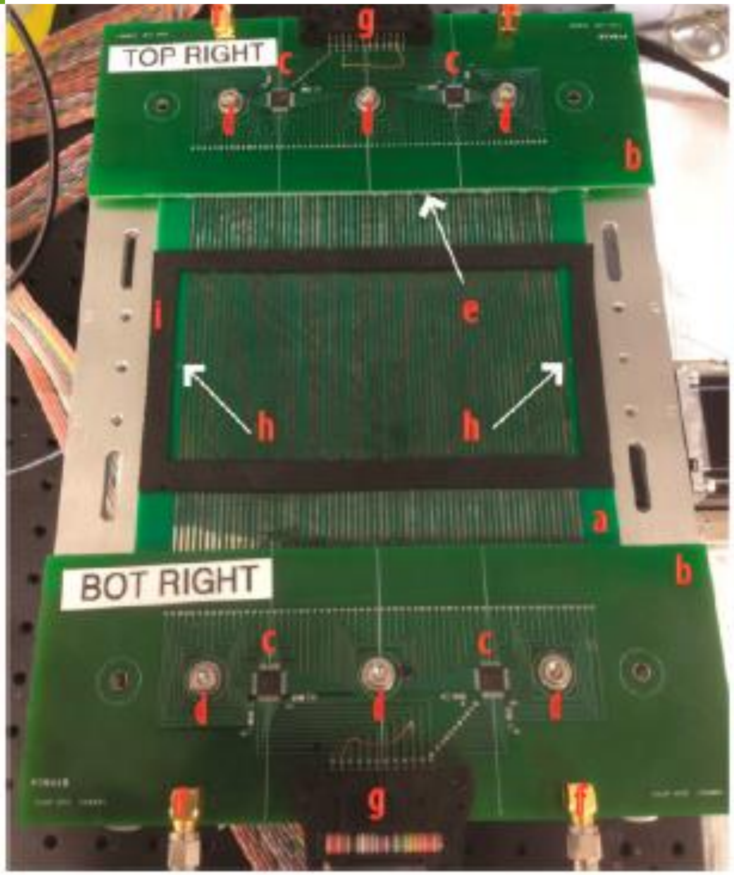


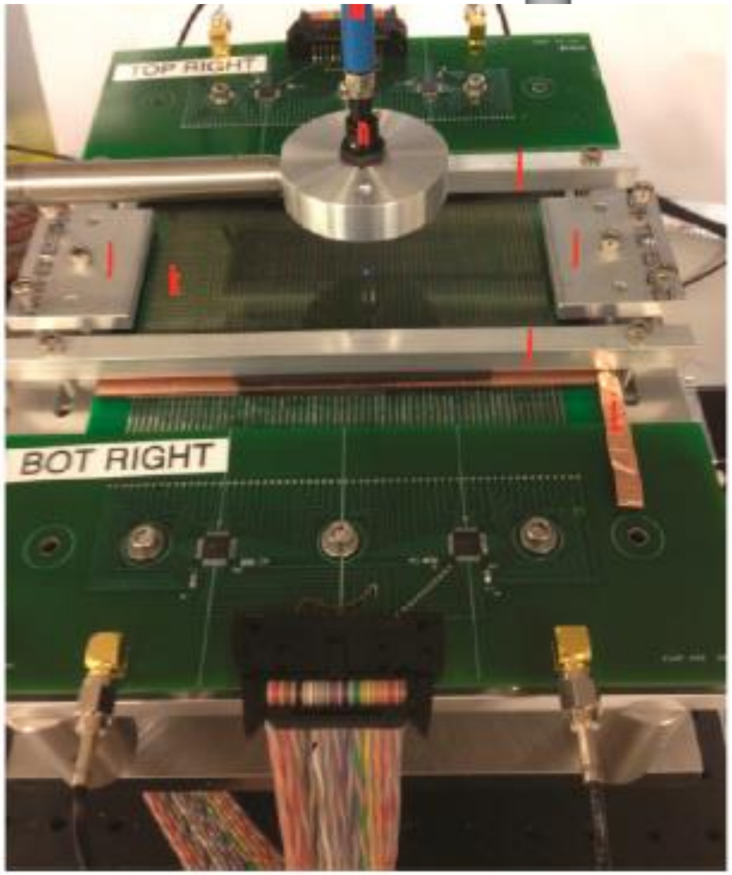
Primary PEC Screen for Photoabsorbers: Quantum Efficiency

Materials synthesis → Light-absorber screening / Electrocatalyst screening

- Colorimetry
- Optical Band Gap
- **Quantum Efficiency**
- Aqueous Echem.







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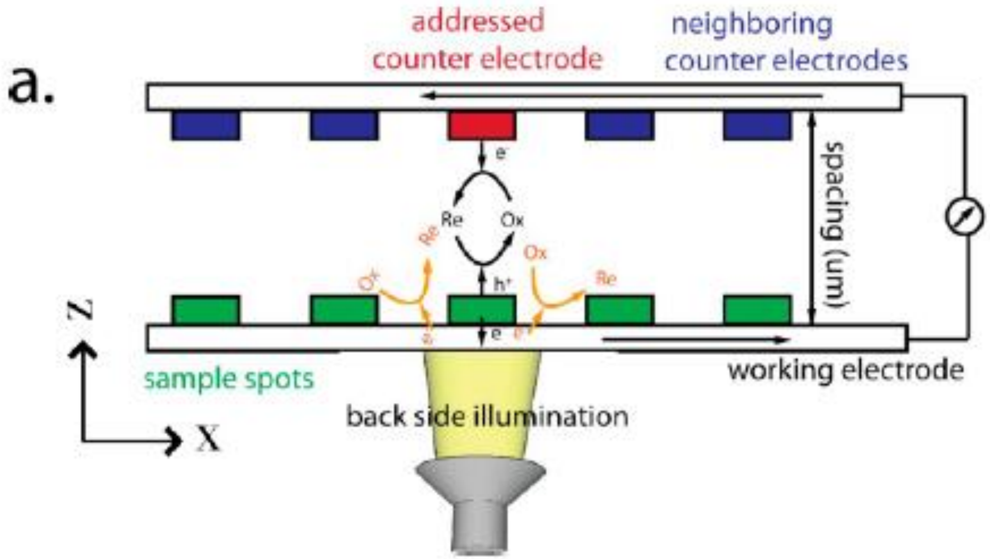
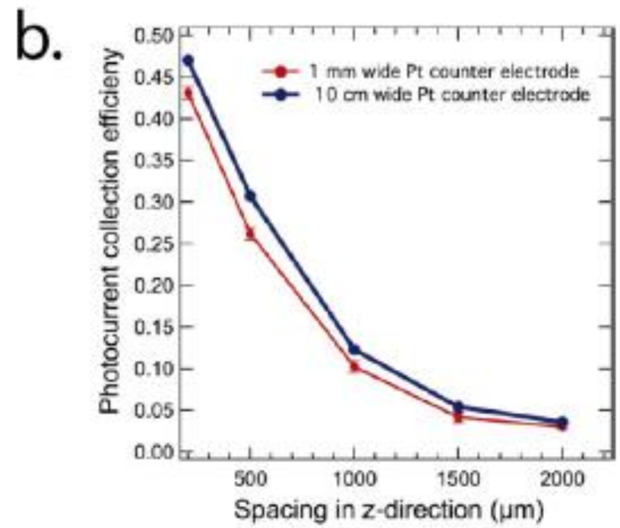
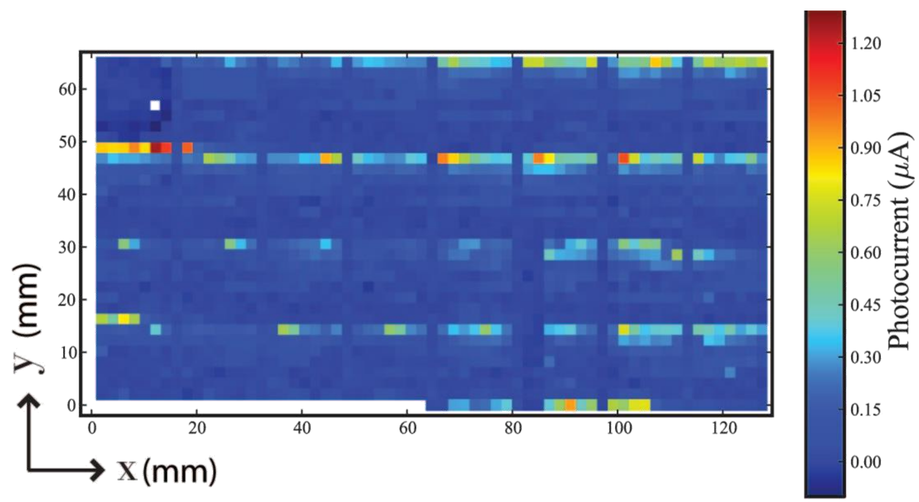
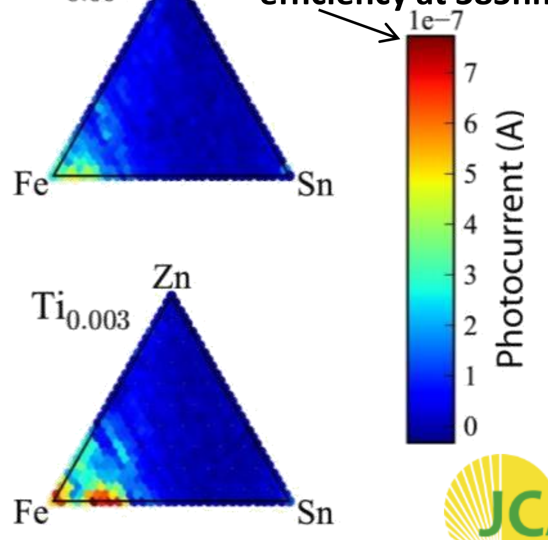
Mapping 2-electrode photocurrent





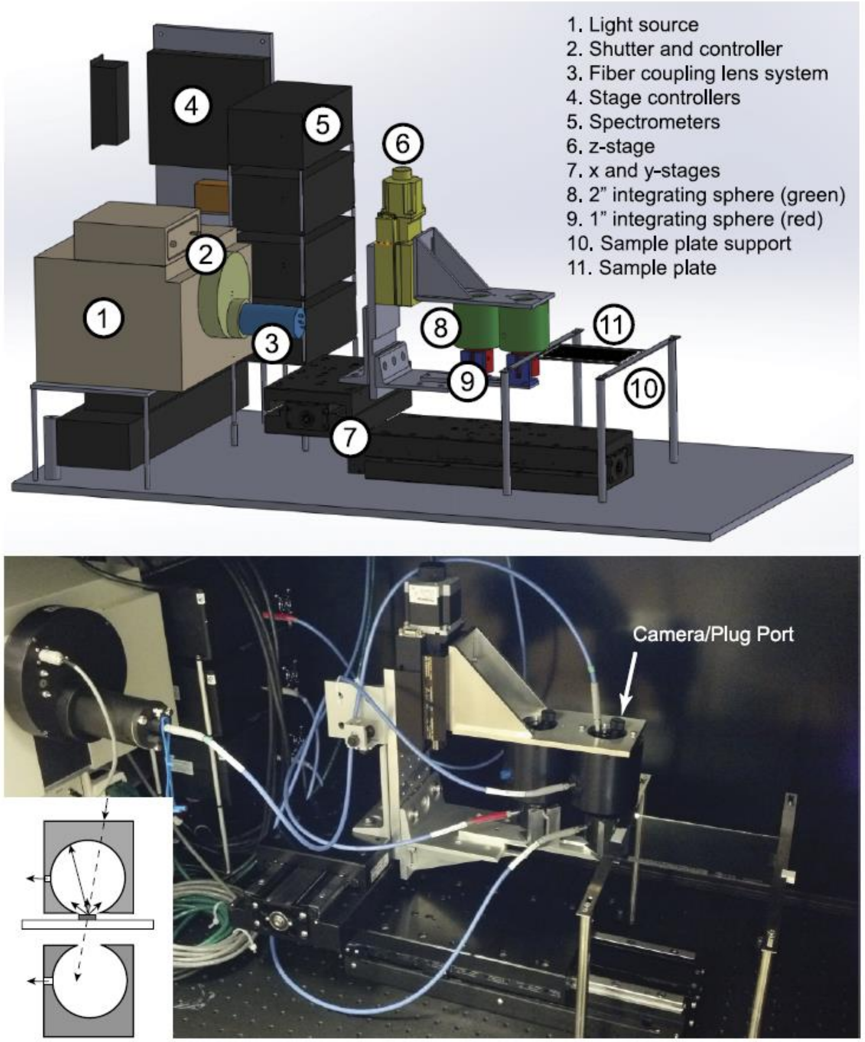


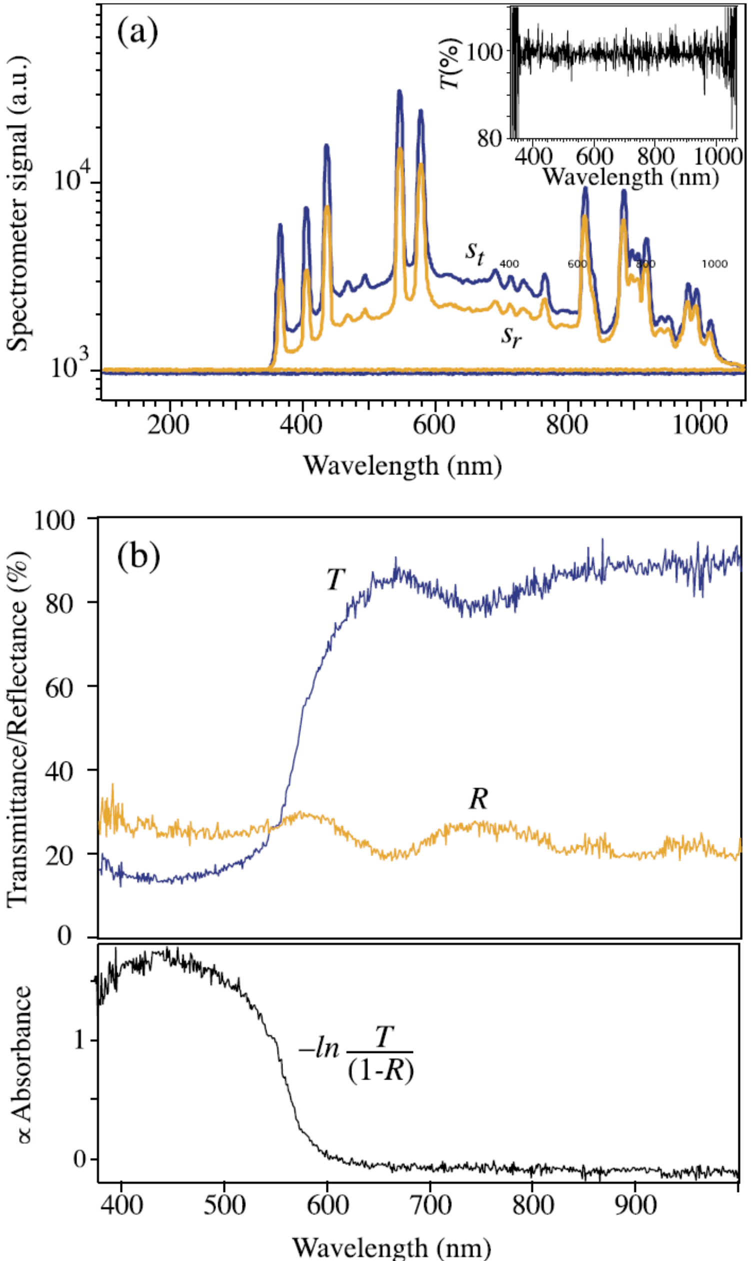
4% Quantum efficiency at 385nm



Xiang, C., Haber, J., Marcin, M., Mitrovic, S., Jin, J., & Gregoire, J. M. (2014). Mapping Quantum Yield for (Fe-Zn-Sn-Ti)Ox Photoabsorbers Using a High Throughput Photoelectrochemical Screening System. *ACS Comb Sci*, *16*, 120–127.

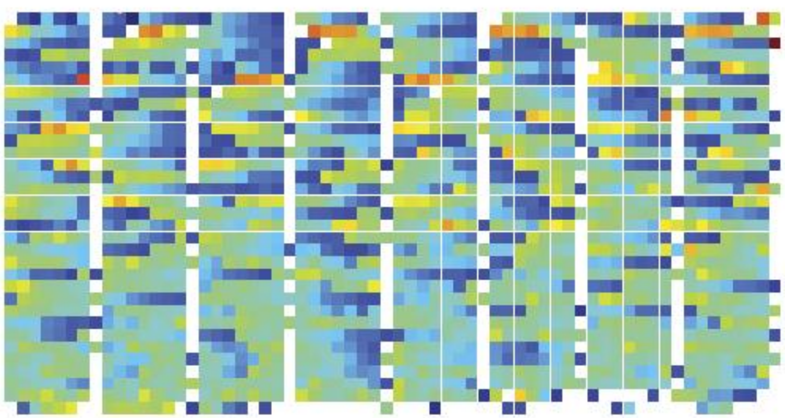
On-The-Fly UV-Vis Spectroscopy

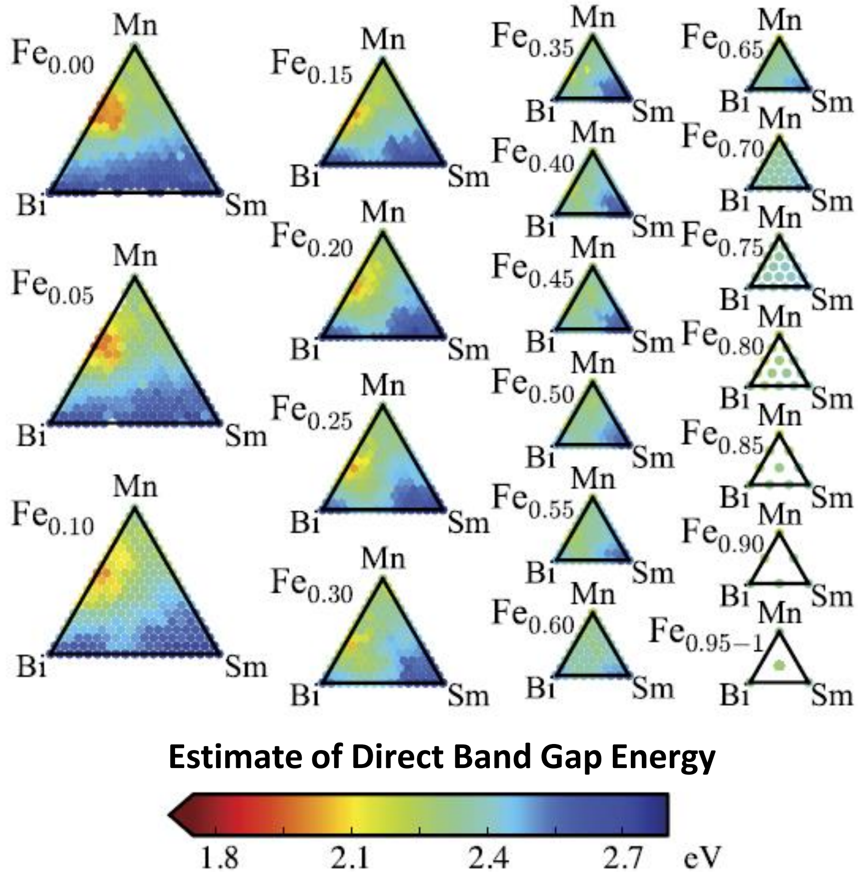




S. Mitrovic, E. W. Cornell, M. R. Marcin, R. J. R. Jones, P. F. Newhouse, S. K. Suram, J. Jin and J. M. Gregoire, "High-throughput on-the-fly scanning ultraviolet-visible dual-sphere spectrometer" Rev. Sci. Instrum. 86, 013904 (2015).

On-The-Fly UV-Vis Spectroscopy: Example band gap mapping





S. Mitrovic, E. W. Cornell, M. R. Marcin, R. J. R. Jones, P. F. Newhouse, S. K. Suram, J. Jin and J. M. Gregoire, "High-throughput on-the-fly scanning ultraviolet-visible dual-sphere spectrometer" Rev. Sci. Instrum. 86, 013904 (2015).

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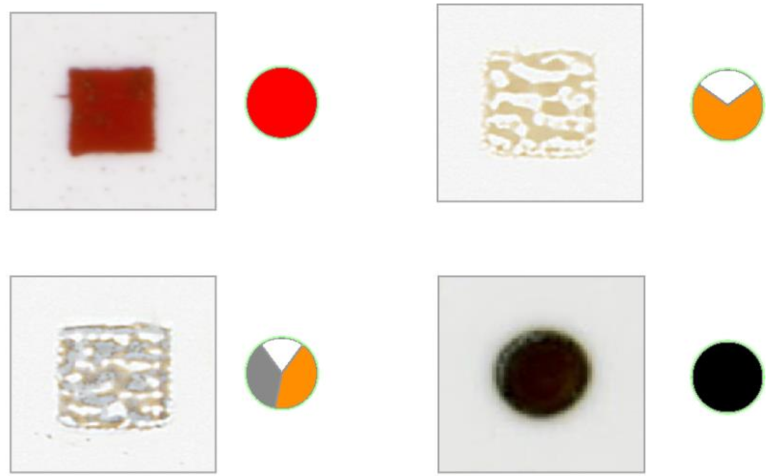
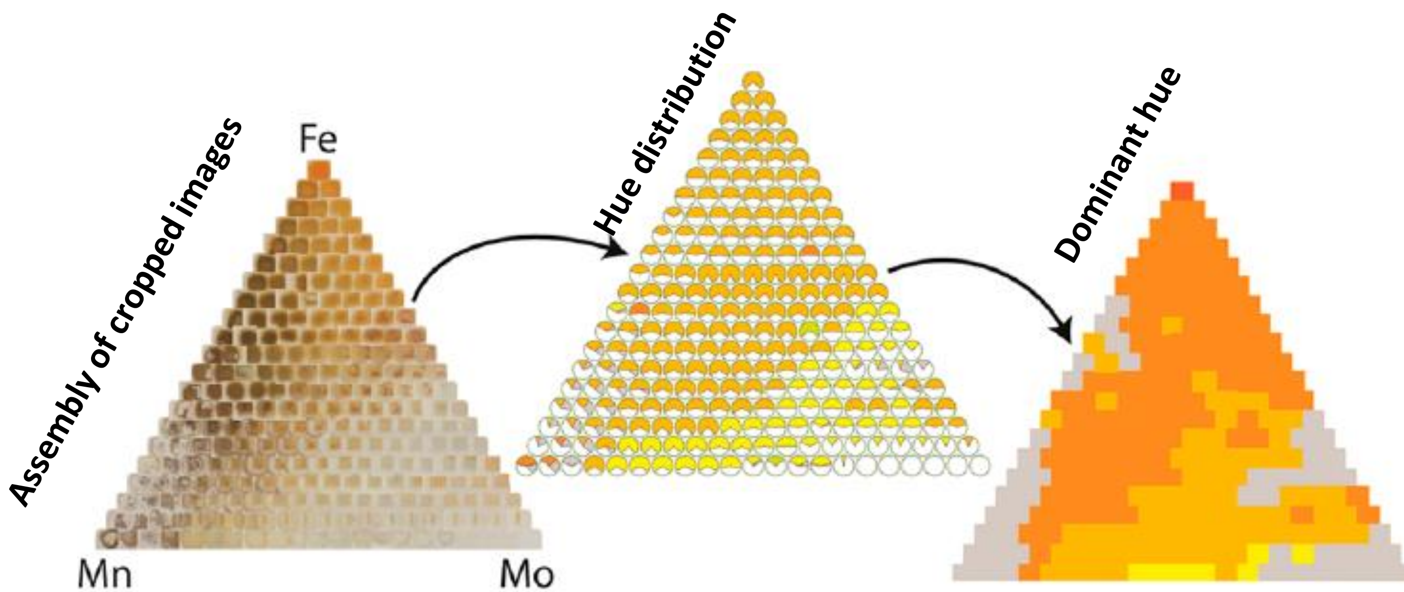
Optical characterization

Colorimetry





S. Mitrovic, E. Soedarmadji, P. F. Newhouse, S. K. Suram, J. a. Haber, J. Jin and J. M. Gregoire, "Colorimetric screening for high-throughput discovery of light absorbers." ACS Combinatorial Science (2014).

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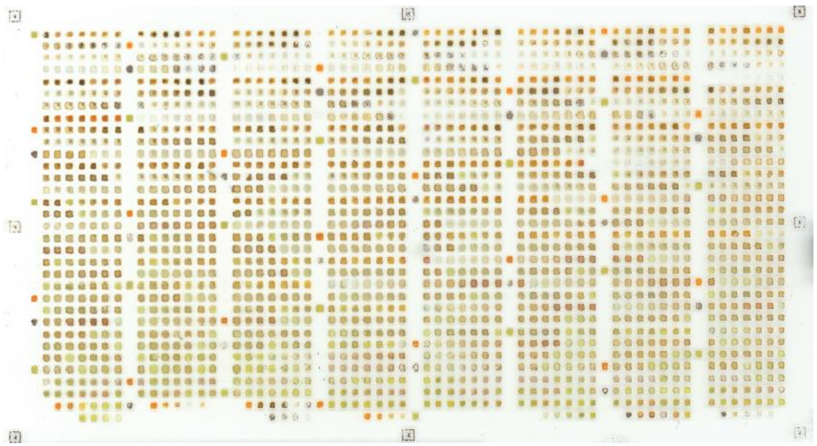
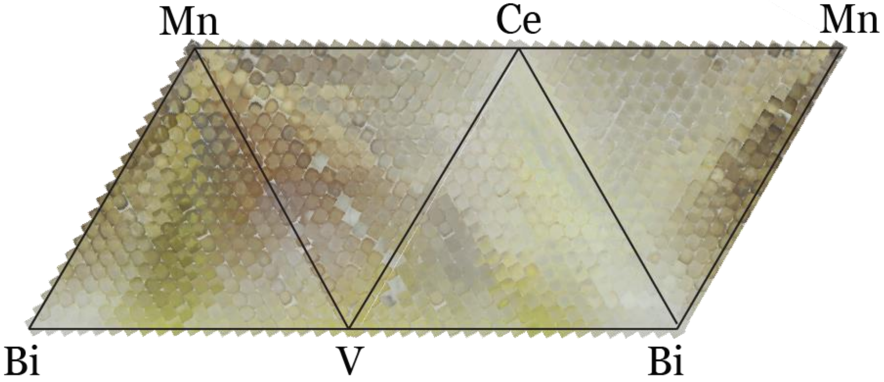
Comparison of Optical Screening Data

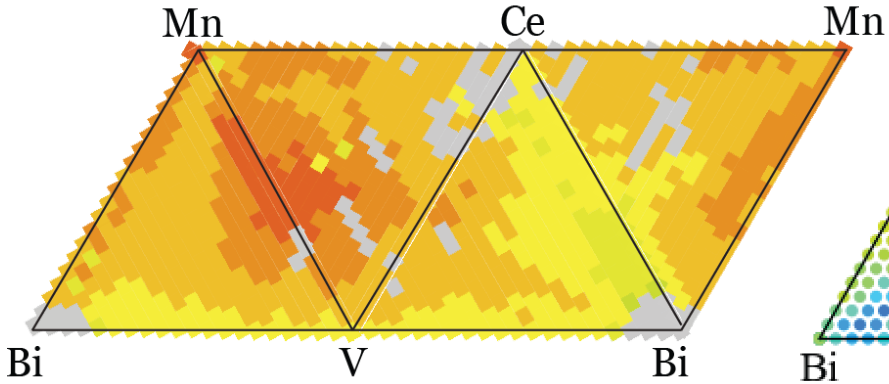
Scanner Image



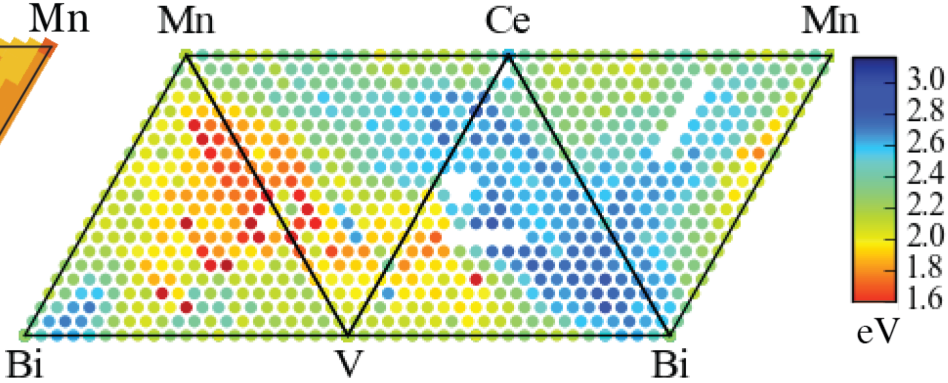
Reconstructed Images for Ternaries



Dominant Hue



Estimated Optical band gap from UV-Vis



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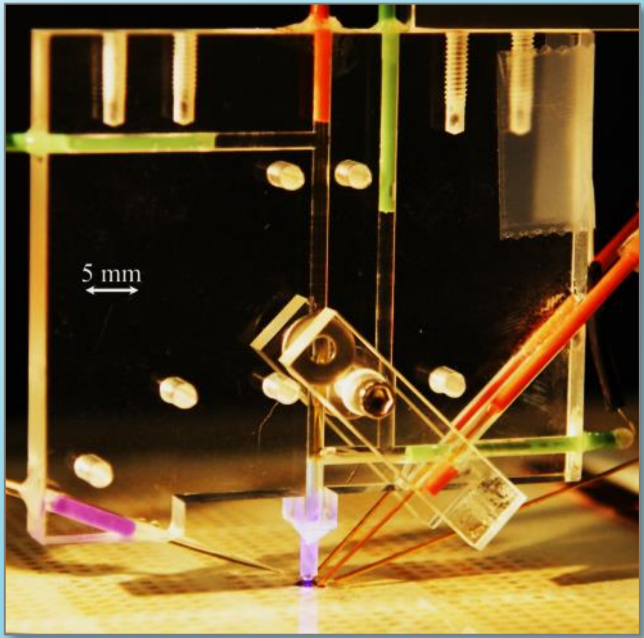
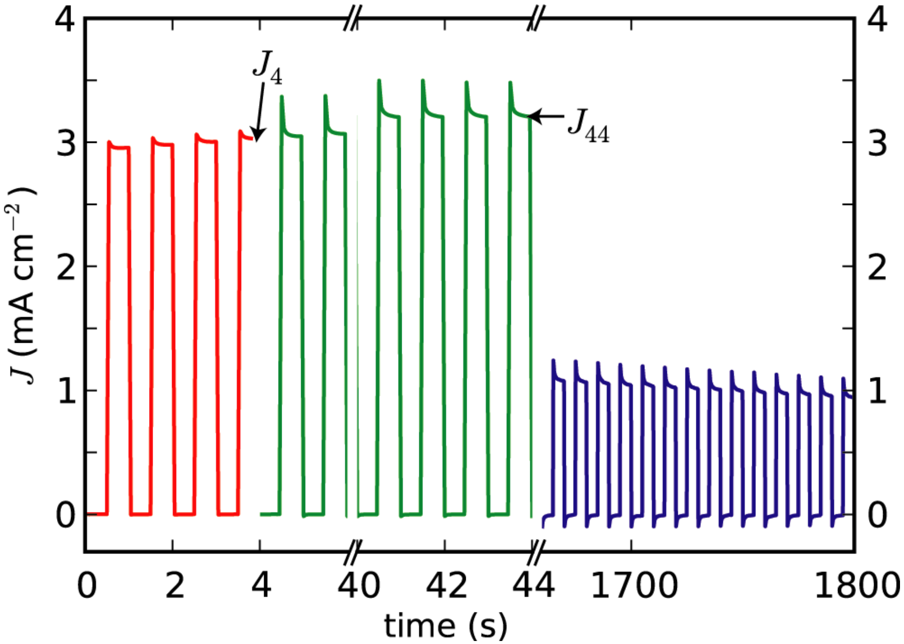
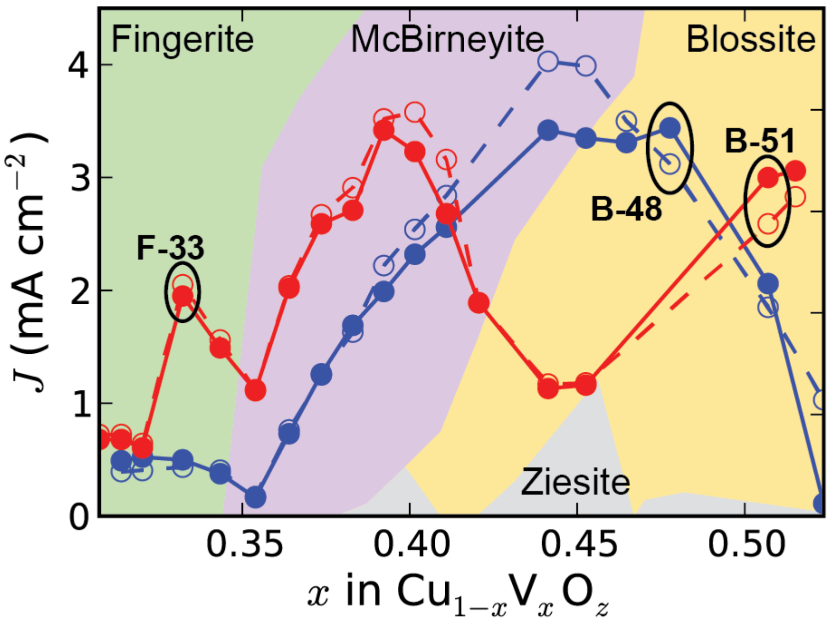
SDC Photoelectrochemistry

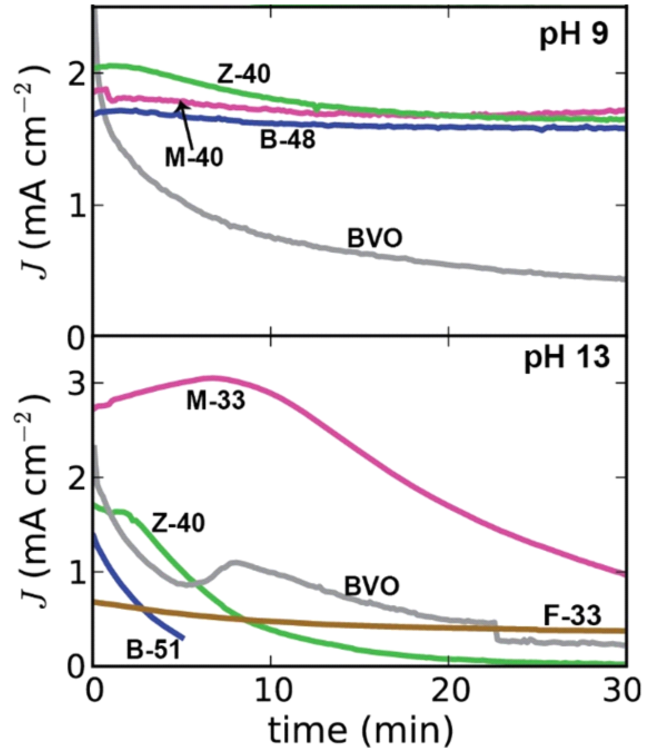
Scanning Droplet Cell (SDC) *

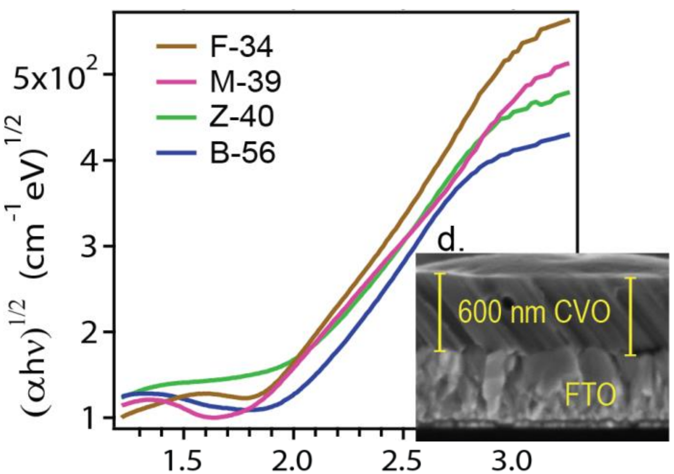




Discovery of CuO-V2O5 Solar Fuels Photoanode





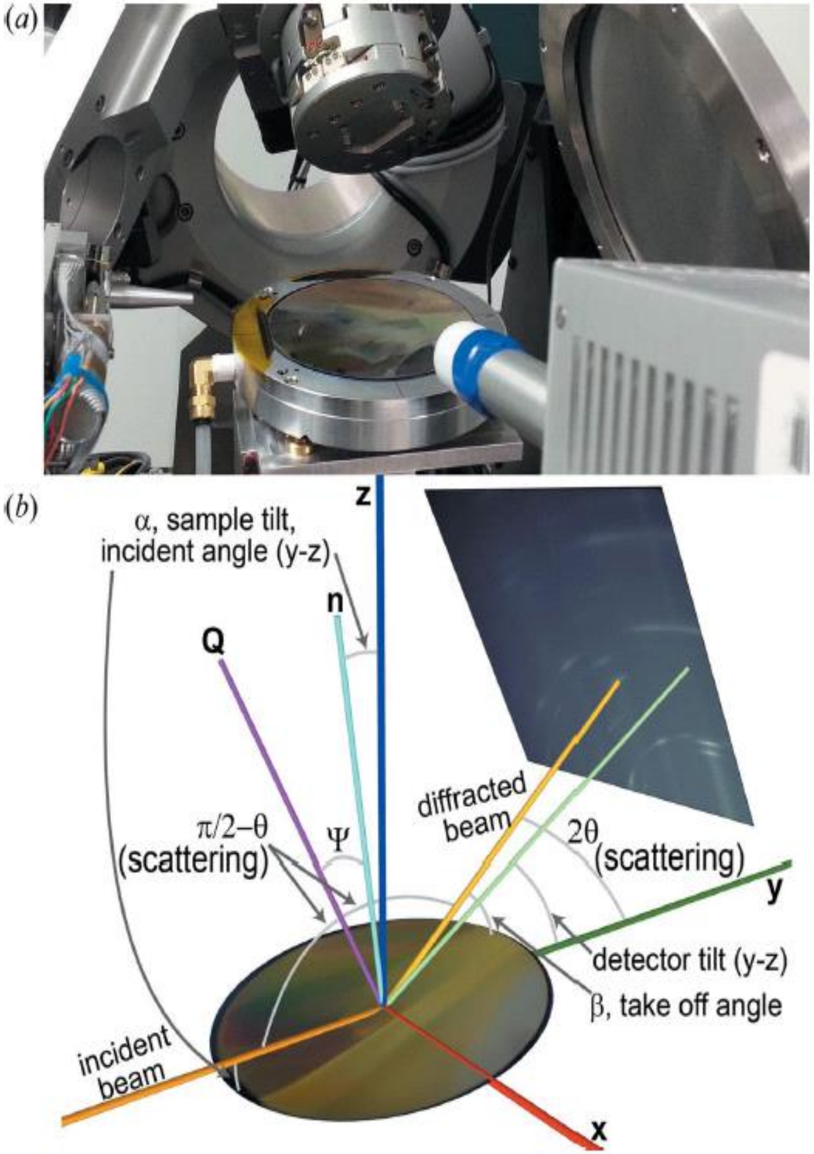


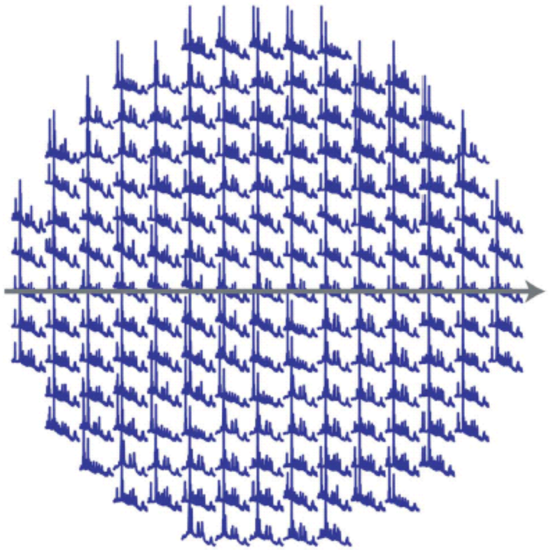
- 4 phases with (indirect) band gap near 2 eV
- Considerable OER photocurrent in alkaline solution
- 2 phases in pH 13 and 4 phases in pH 9 with better stability than BVO
- Excellent agreement between measured and calculated band gaps

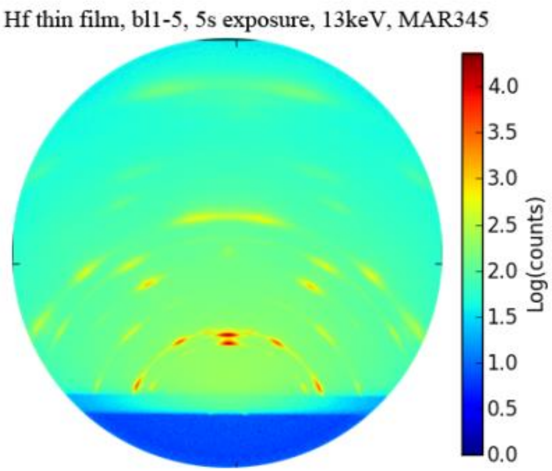
L. Zhou, Q. Yan, A. Shinde, D. Guevarra, P. F. Newhouse, N. Becerra-Stasiewicz, S. M. Chatman, J. A. Haber, J. B. Neaton, J. M. Gregoire, Advanced Energy Materials, accepted (2015)

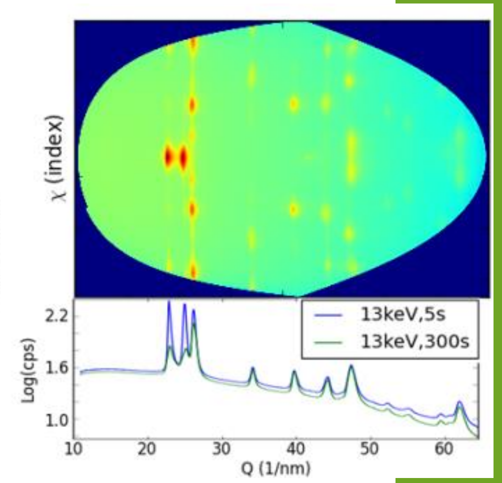
BVO prepared by Francesca Toma, LBNL

HiTp XRD+XRF at SSRL 1-5









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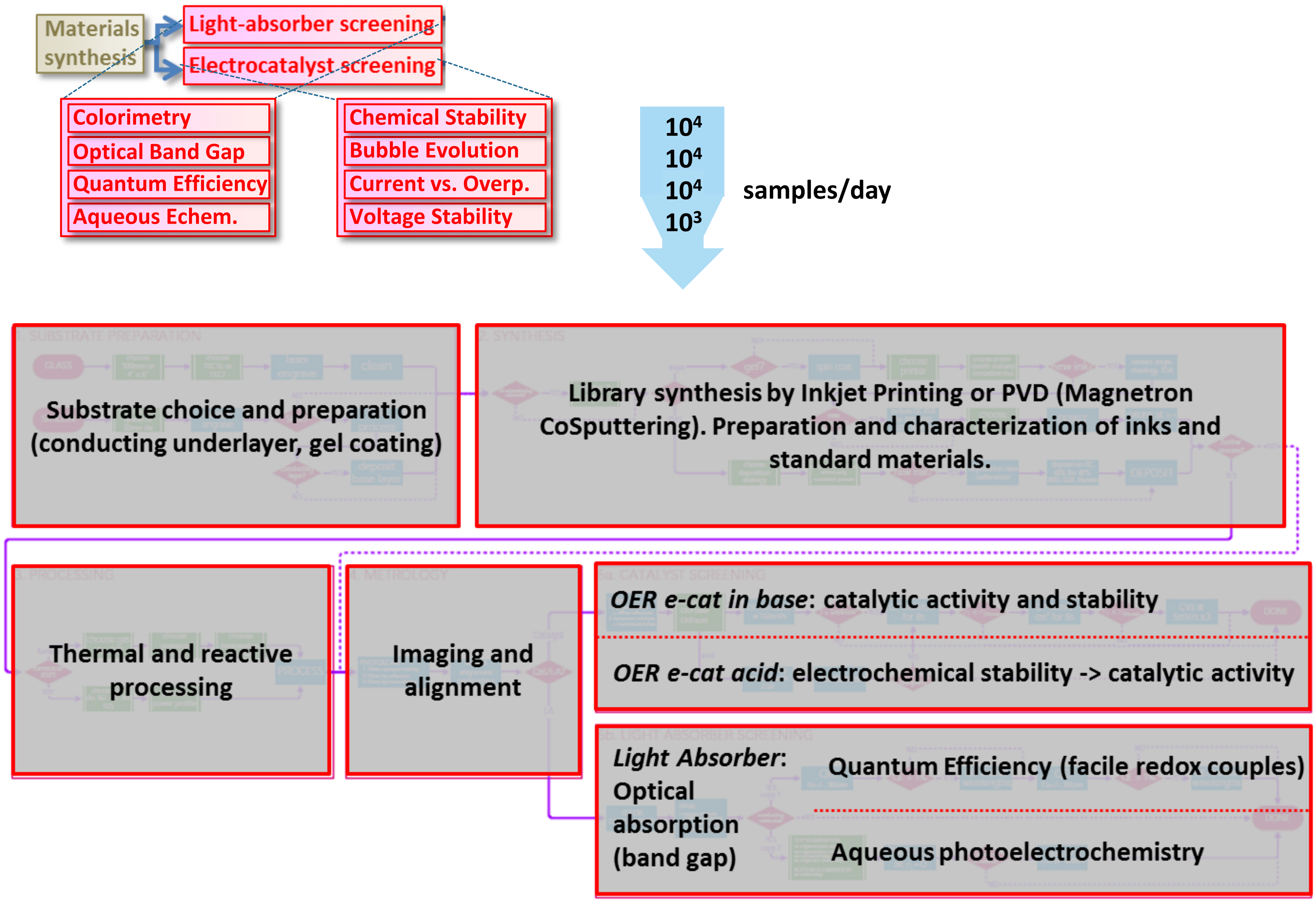
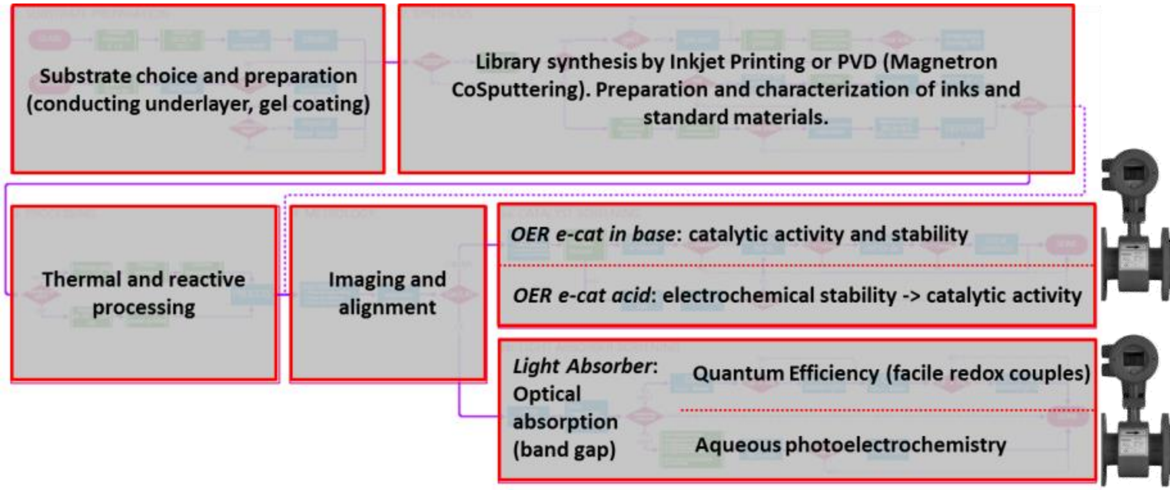
JCAP-HTE Pipeline v1

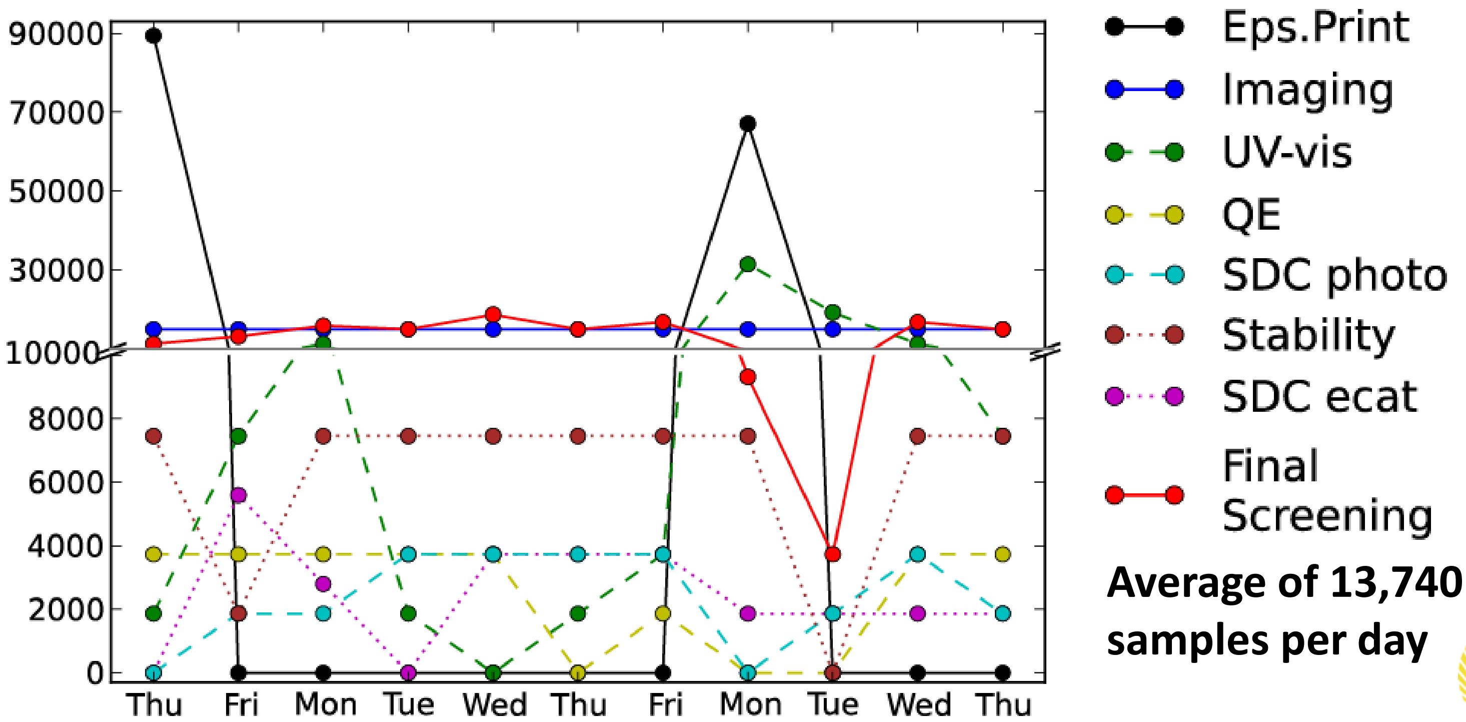
Pipeline v1



Pipeline Operation at 13,740 samples per day



Samples completing "Final Screening" have traversed the entire pipeline

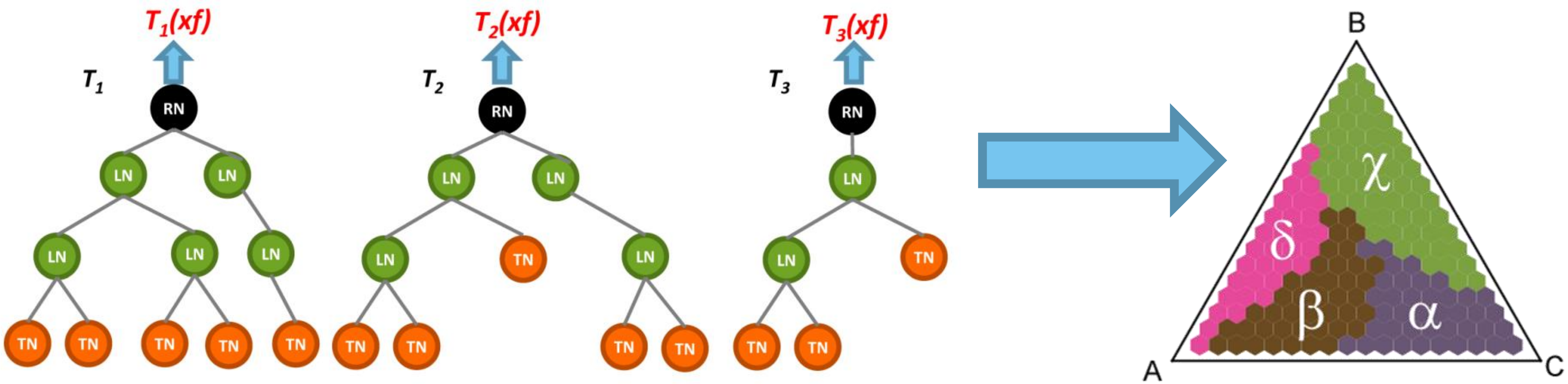


Average of 13,740 samples per day

JCAP Joint Center for Artificial Photosynthesis

Pipeline v1 summary

- **Synthesis and screening of 10^4 materials per day with data comparable to traditional techniques**
  - Could be >10x higher throughput with “smart” down-selection
  - Scientific understanding requires investigation of unique materials, which may or not be high-performance



- **These are automated experiments, but not a robotic science warehouse**
  - Substantial user involvement in operation, quality control and decisions based on scientific intuition

S. K. Suram, J. a. Haber, J. Jin and J. M. Gregoire, "Generating Information Rich High-Throughput Experimental Materials Genomes using Functional Clustering via Multi-Tree Genetic Programming and Information Theory" ACS Combinatorial Science 17 (4), 224-233 (2015).

The Joint Center for Artificial Photosynthesis (JCAP) is the nation's largest research program dedicated to the development of an artificial solar-fuel generation technology. Established in 2010 as a U.S. Department of Energy (DOE) Energy Innovation Hub, JCAP aims to find a cost-effective method to produce fuels using only sunlight, water, and carbon-dioxide as inputs. JCAP is led by a team from the California Institute of Technology (Caltech) and brings together more than 140 world-class scientists and engineers from Caltech and its lead partner, Lawrence Berkeley National Laboratory. JCAP also draws on the expertise and capabilities of key partners from the University of California campuses at Irvine (UCI) and San Diego (UCSD), and the Stanford Linear Accelerator (SLAC). In addition, JCAP serves as a central hub for other solar fuels research teams across the United States, including 20 DOE Energy Frontier Research Center.

For more information, visit http://www.solarfuelshub.org.

Computational work is supported by the Materials Project Predictive Modeling Center (EDCBEE) through the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, under Contract No. DE-AC02-05CH11231. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02–05CH11231.