Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials

Eric W. McFarland (PI), University of California, Santa Barbara

DOE Hydrogen Program DE-FC36-01GO11092

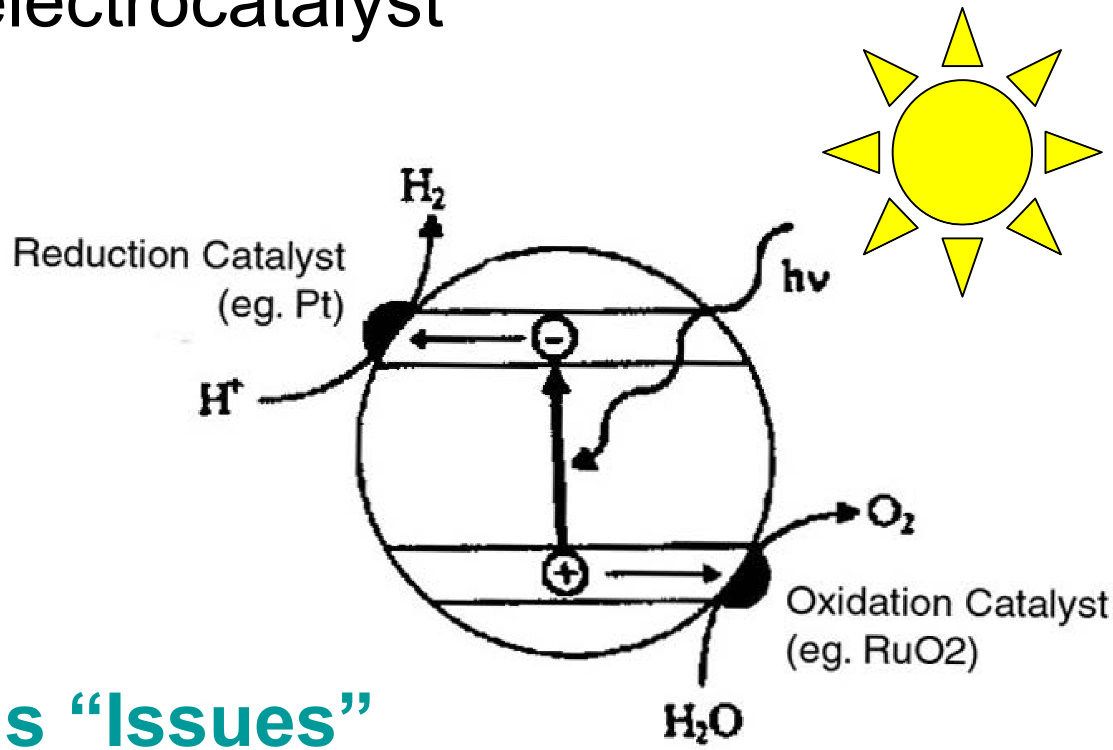
Primary Objective:

Discovery of efficient, practical, and economically sensible new materials for photoelectrochemical production of hydrogen from water and sunlight.

Methodology:

Apply combinatorial methods to complement the traditional research paradigm of serial “deductive” chemical research with a deliberate, high-speed, “inductive” exploration of the composition-structure-property relationships of new metal-oxide based solid-state materials.

Photoelectrocatalyst

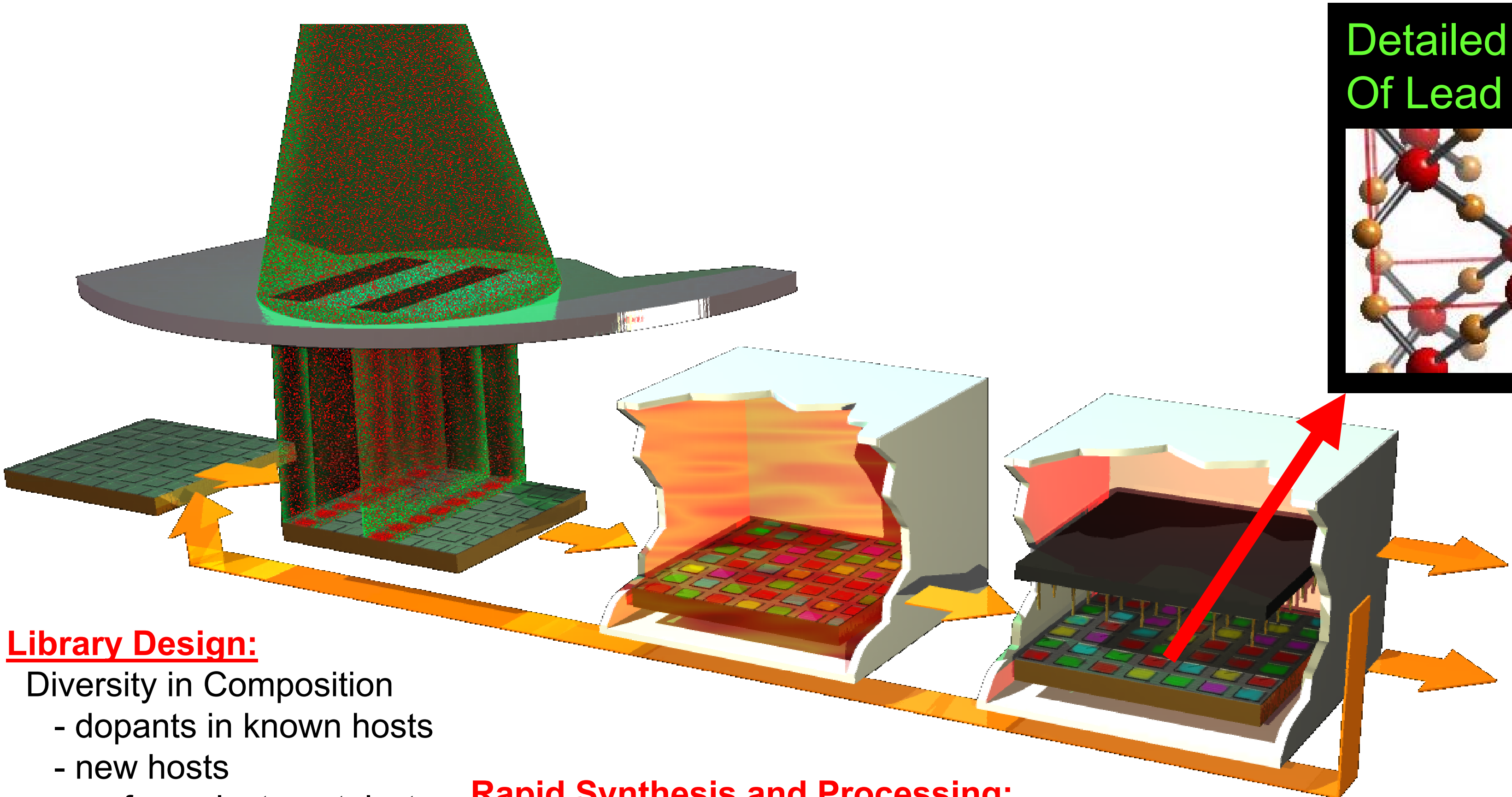


Materials "Issues"

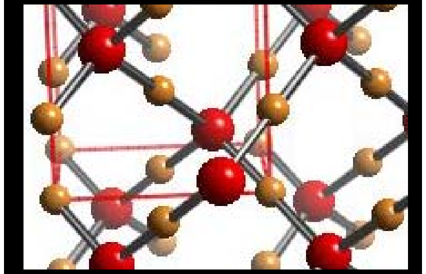
- Absorbance
- Transport e-/h+
- Surface Electrocatalysis
- Band Structure Energetics
- Stability and Cost

Bulk Particulates ~ **Structural Photoelectrodes**

Combinatorial Approach: Paradigm Shift



Detailed Analysis Of Lead Materials



Library Design:

Diversity in Composition
- dopants in known hosts
- new hosts
- surface electrocatalysts

Diversity in Synthesis
- structure variability
- surfactant templates

Rapid Synthesis and Processing:

Electrochemical Deposition
Electroless Deposition
Parallel Reactor Blocks
Rapid Serial Scanning Cells
Pyrolysis

High-Throughput Screening:

Photoelectrochemical
Chemo-Optical

Relevance:

- **The materials will be active electrocatalysts stable in electrolytes.**
  - *Dual use applications in electrolysers and fuel cells.*

- **They will have efficient solar spectrum absorbance and efficient electron/hole conduction properties.**
  - *Dual use in photovoltaic applications.*

- **May be economically incorporated in reactor designs using photoelectrodes or bulk slurry particulates.**
  - *Dual use in environmental photocatalysis*.

- **New metal oxide materials developed in this program will be inexpensive in bulk quantities.**

  $\Rightarrow$ ***Primary Use In Cost Competitive Large Scale Hydrogen Production***

Materials Developed As Part of This Research Have Broad Applications In the US Energy Program

Project Timeline (Start Date September 2001)

Sept. 01 | Sept. 02 | Sept. 03 | Sept. 04

System(s):

- Automated Electrodeposition (Task Y1-1)
- Automated Pyrolysis
- Electro-Optical Screening (Task Y1-5)
- Electrochemical Screening (Task Y1-3)
- Optical Band Gap Screening (Y2-4)

Synthesis :

- Generalized Synthesis Chemistry (Task Y1-2)
- Validation Libraries - ZnO (Task Y1-4) | ZnO (Y2-2) | ZnO (Y3)
- AxByCzO Libraries (TaskY1- 6) | AxByCzO Libraries (Y2- 1) | AxByCzO Libraries (Y3)
- Heterostructure Libraries (Task Y2- 6)
- Mesoporous Libraries (TaskY1- 7) | Mesoporous Libraries (Y2- 7) | Mesoporous Libraries (Y3)
- Electrocatalysis Libraries (Y2-3) | Electrocatalysis Libraries (Y3)
- Electroless WOMxO

Screening and Detailed Quantitative Analysis:

- Validation Libraries (Task Y1-4, 9) | ZnO (Y2-2) | ZnO (Y3)
- AxByCzO Libraries (Task Y1-6,9) | AxByCzO Libraries (Y2- 1) | AxByCzO Libraries (Y3)
- Mesoporous Libraries (Y2- 7) | Mesoporous Libraries (Y3)
- Electrocatalysis Libraries (Y2-3) | Electrocatalysis Libraries (Y3)

Data Management:

- Database Structure (Task Y1-8)
- Software and Data Implementation

Outreach and Tech Transfer:

- Adrena Inc/SBA Materials
- IEA Annex 14
- Research Publications - 10 published papers
- 2 Patent Applications (mesoporous MOx, Pt/WO3 Fuel Cell Cat)

Significant Results To Date

- Design and fabrication of combinatorial chemistry ***systems for synthesis and screening of hydrogen producing photocatalysts.***

- Demonstrated that ***compositional and preparative modifications of known metal oxide hosts may improve their photoelectrocatalytic properties***. (WO_3 with ZB visible band photolysis, ZnO:X with improved visible band absorbance and improved stability)

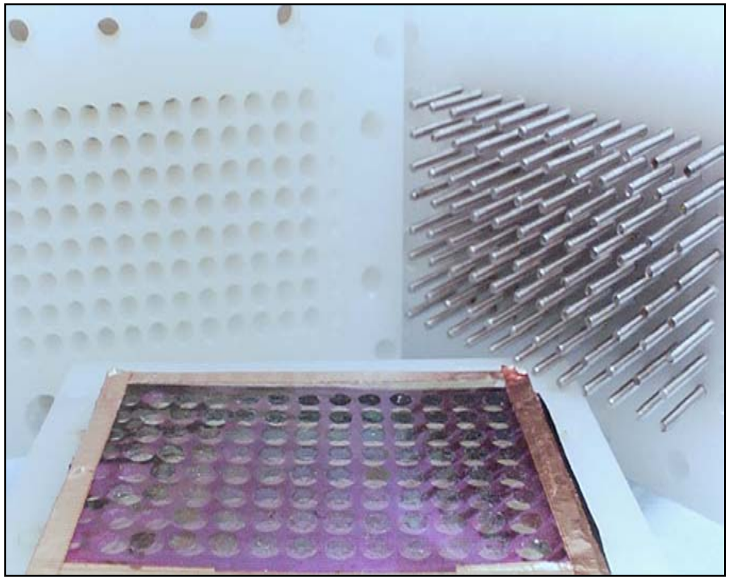
- First ***electrochemical synthesis of ordered nanoporous metal oxides*** *(Patent Assigned to SBA Materials)*

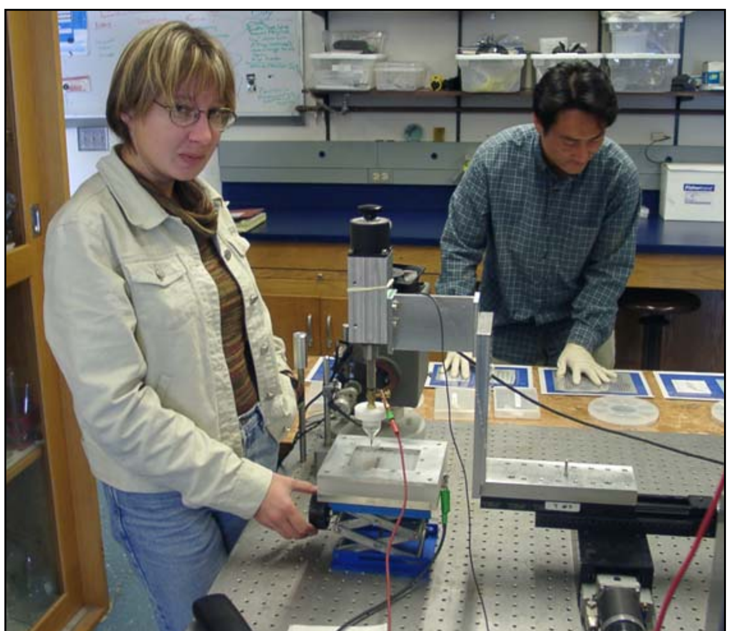
- First ***electroless synthesis of functional metal oxide*** materials and nanoporous frameworks.

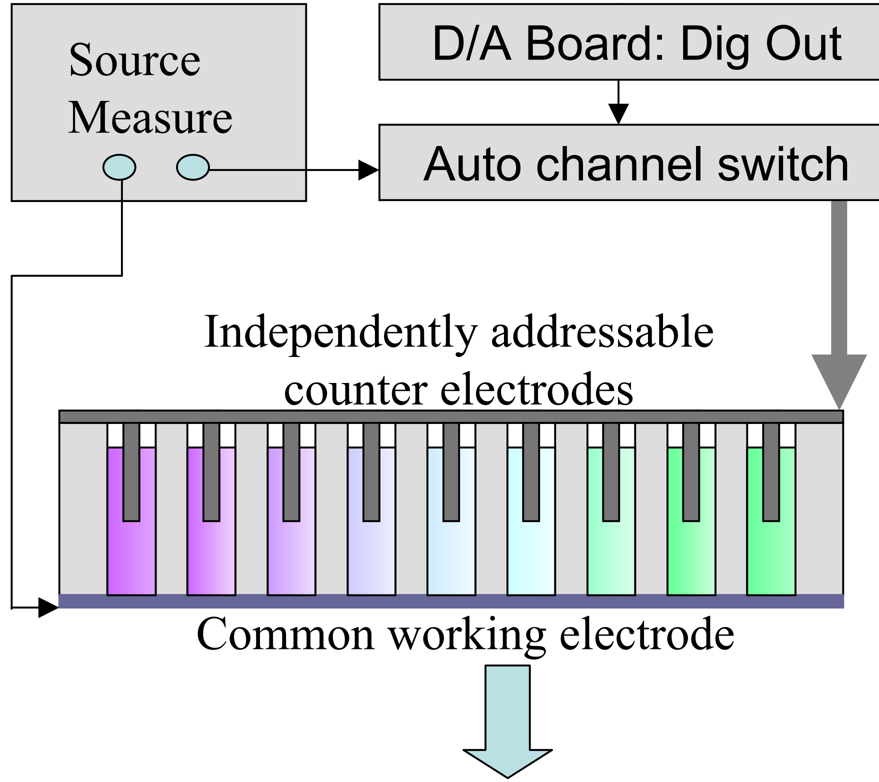
- Discovery of ***nanoparticulate Pt/WO_3 which is photoactive and resistant to CO poisoning*** and controlled electrosynthesis of high activity ***Au nanoclusters.***

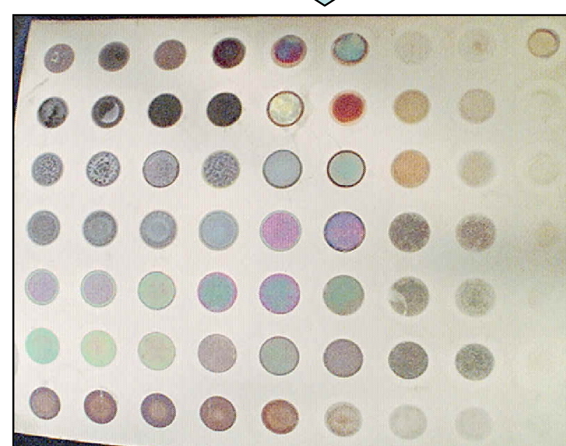
- Identification of ***H intercalation as critical component of poisoning resistance*** of metal oxide electrocatalysts.

Parallel Synthesis

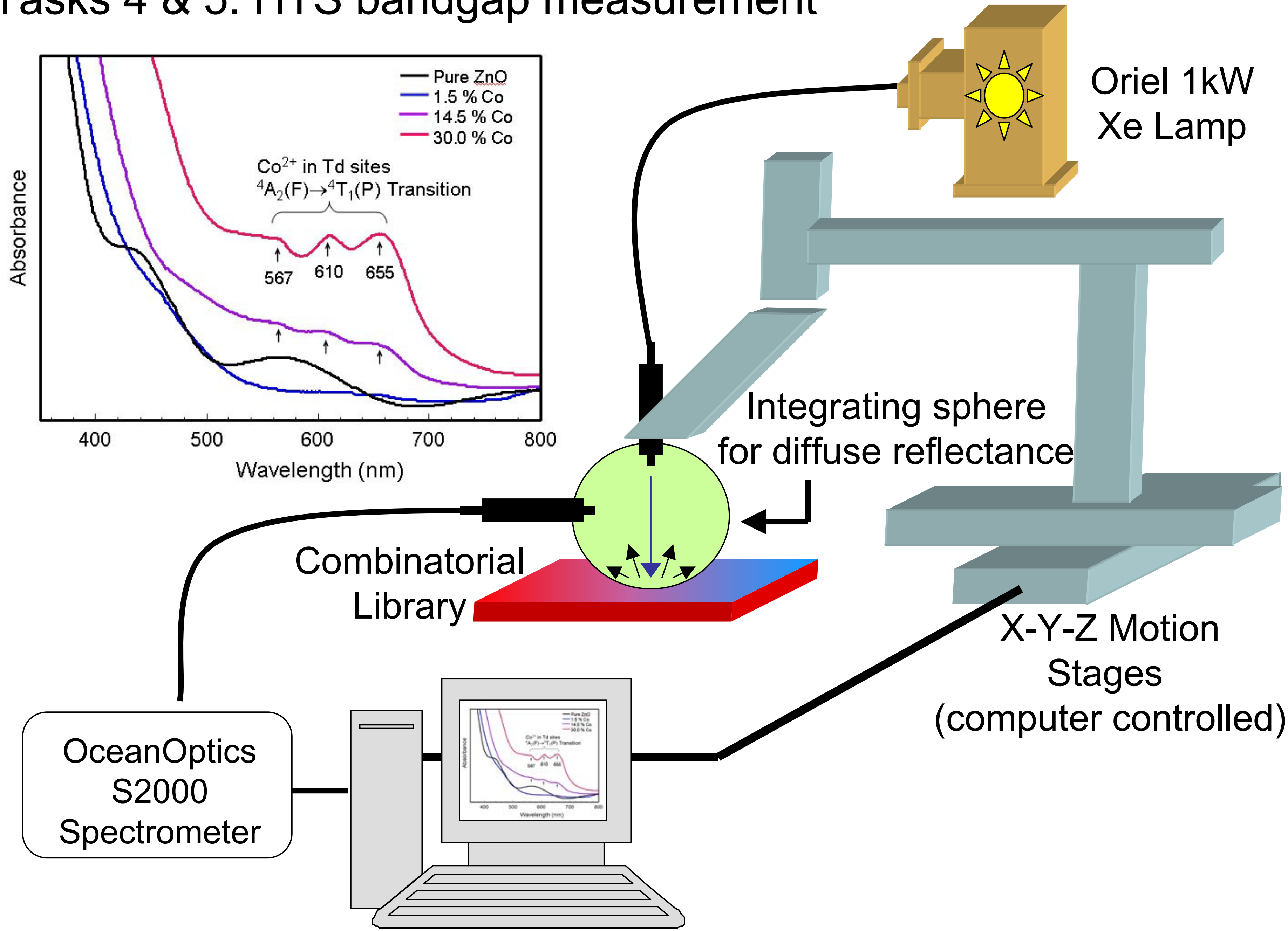








Tasks 4 & 5: HTS bandgap measurement



Generalized Synthesis Chemistries

Metal deposition/Oxidation	*Metal Oxide Deposition*
$M^+ \rightarrow M \rightarrow MO$	**Aqueous: $M^+ \rightarrow MOH \rightarrow MO$**

1. Metal Electrodeposition

$M^{n+} + n\,e^- \rightarrow M^o$ (Cathodic)

2. Anodization/Anneal

$M^o + H_2O \rightarrow MO + 2\,H^+ + 2\,e^-$

$M^o + O_2 \rightarrow MO$

1. MO Deposition

electrode: $2\,H_2O + 2\,e^- \rightarrow H_2 + 2(OH^-)_{sur}$

$[M^{n+}(\text{ligand})] + n(OH^-)_{sur} \rightarrow M(OH)_n$

ligands (acidic) = peroxide

(basic) = lactate, citrate, ethylene glycol, acetate

2. Dehydration/Anneal

$M(OH)_n \rightarrow MO_{n/2} + {}^{n}/_{2}\,H_2O$

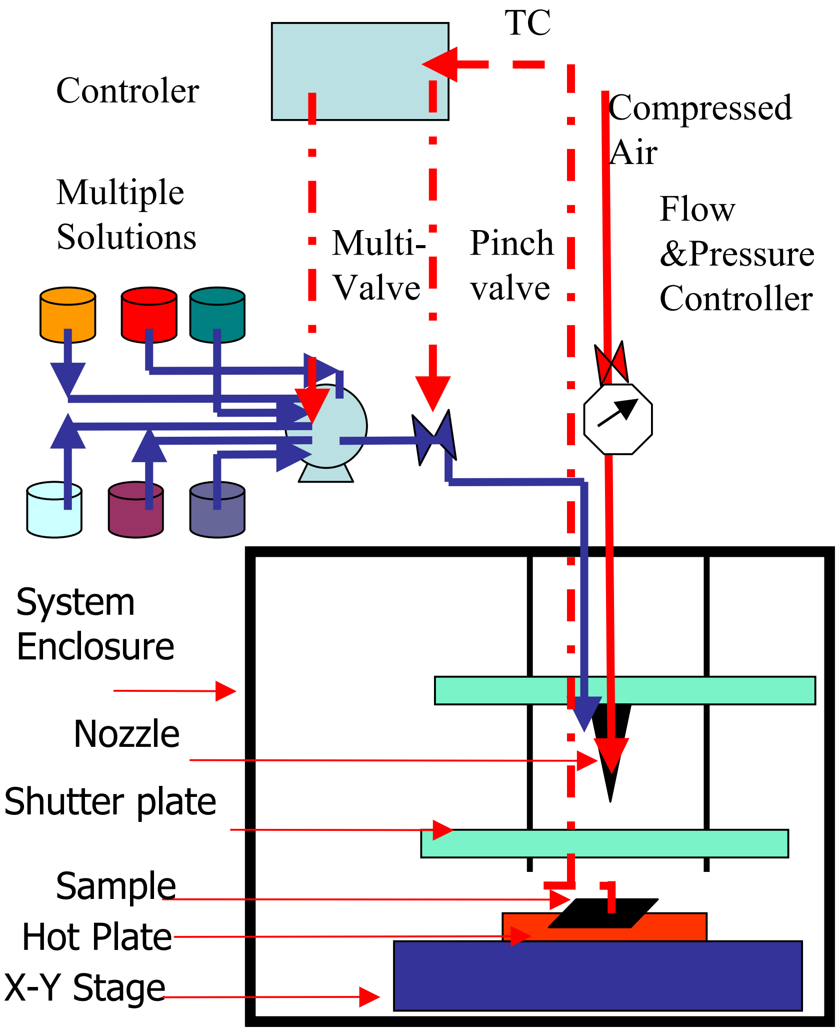
Non-Aqueous: $M^+ + O_2 \rightarrow MO$

1. Direct MO Deposition

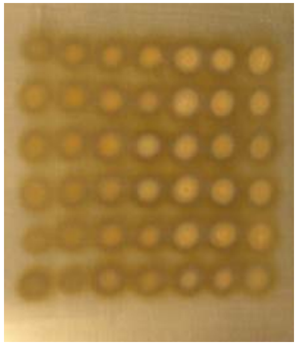
$xM^{n+} + {}^{y}/_{2}O_2 + ne^- \rightarrow M_xO_y$

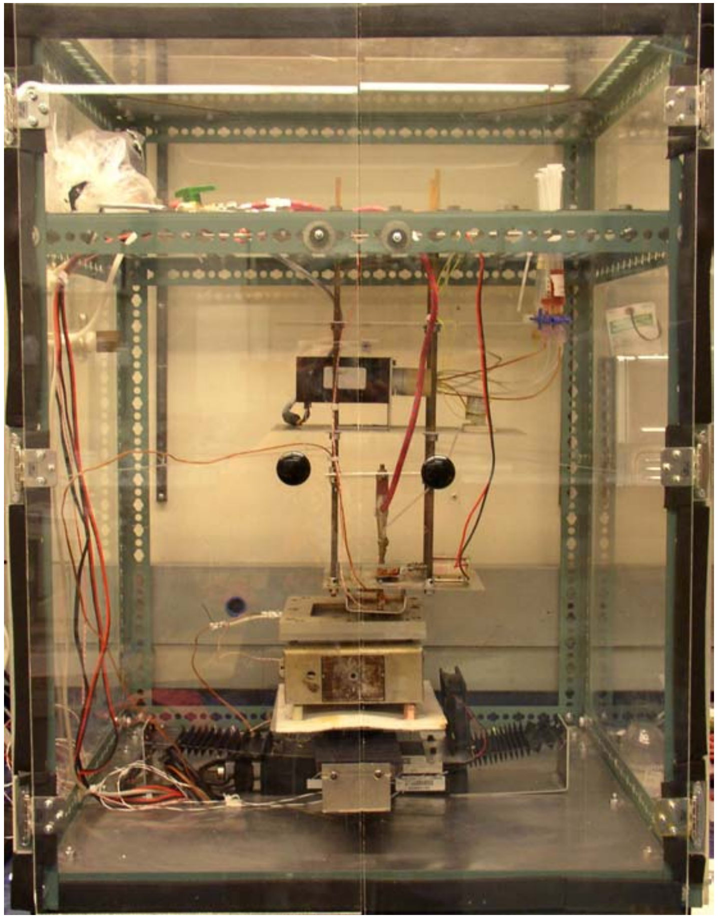
In DMSO etc

Automated Spray Pyrolysis System



Fe_2O_3 Library

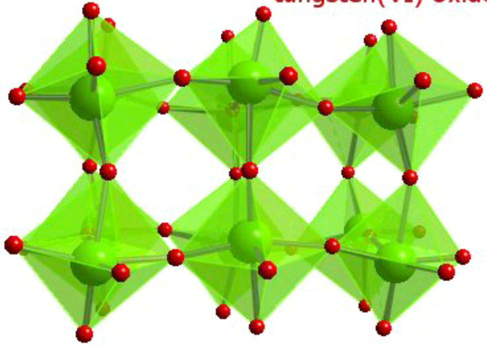


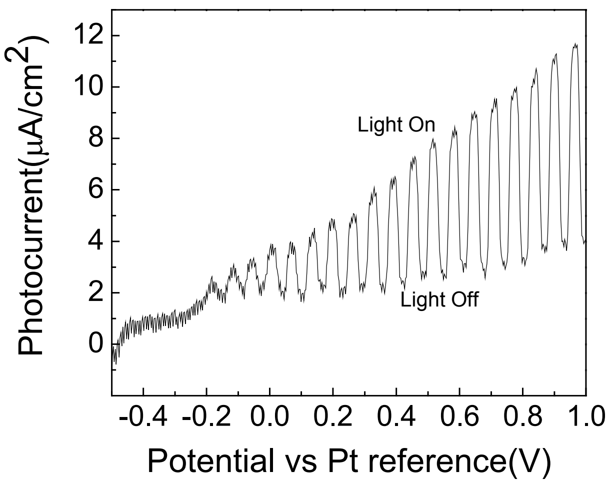


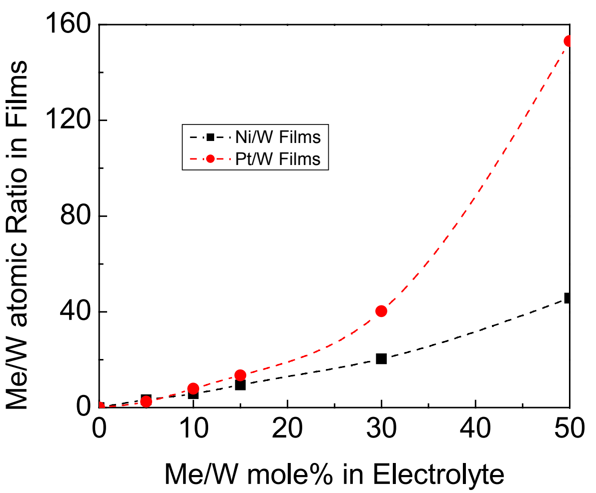
1 meter

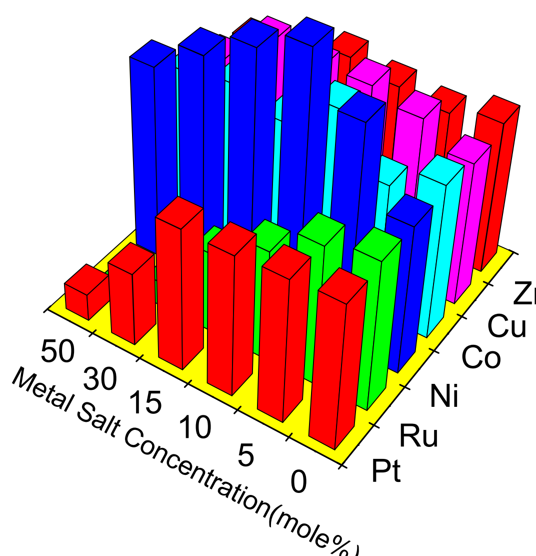
Task 1: Continue WO_3:X - stable, cost effective host

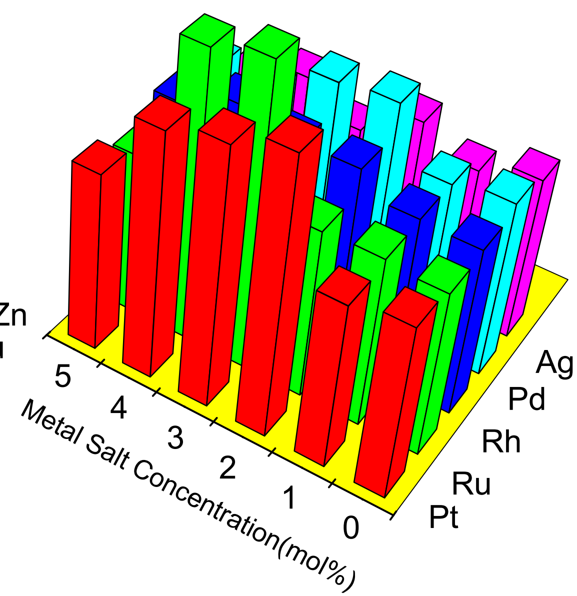
tungsten(VI) oxide

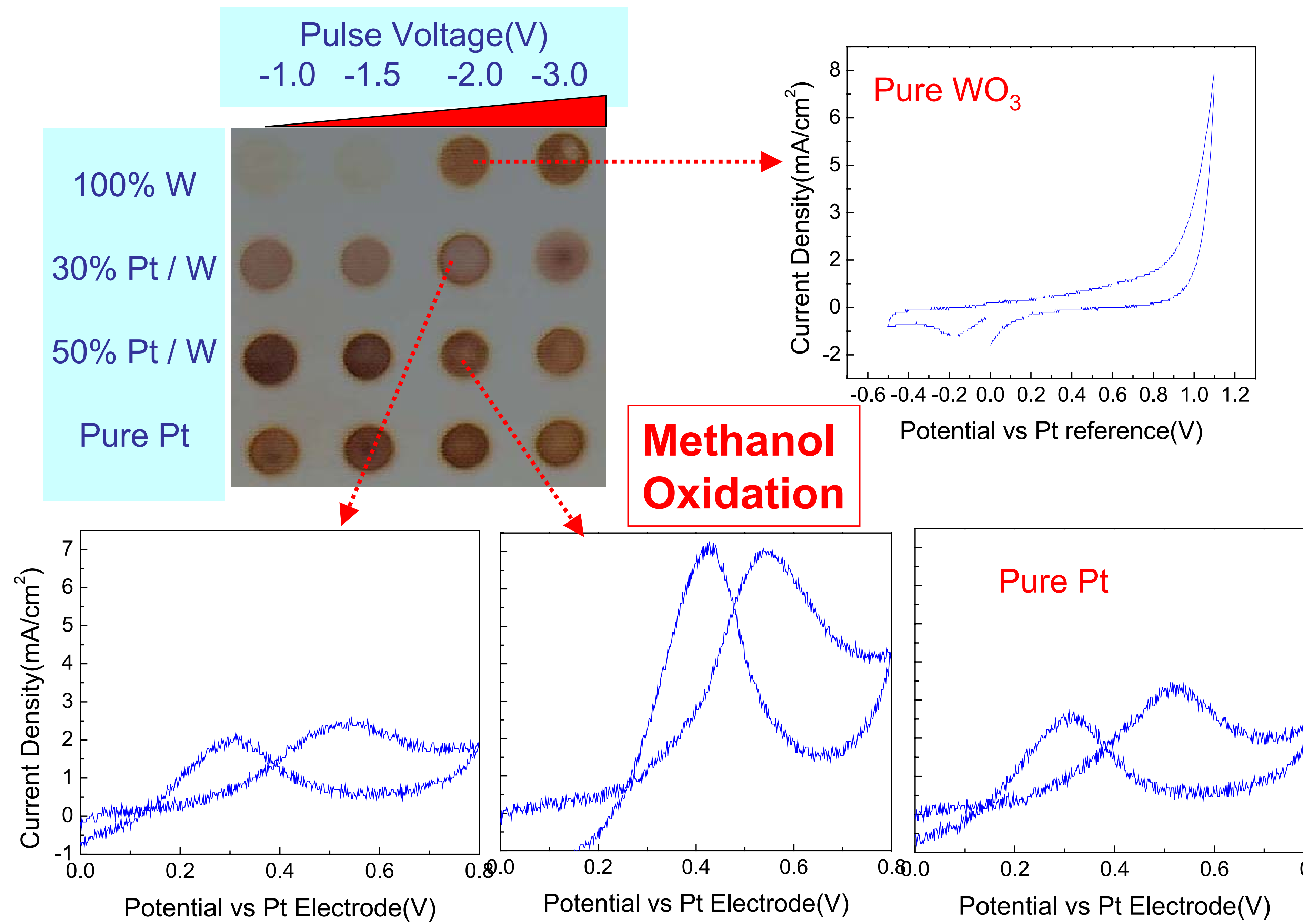






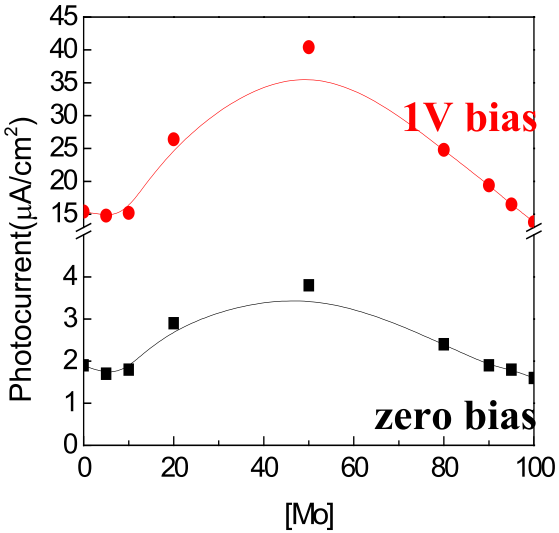




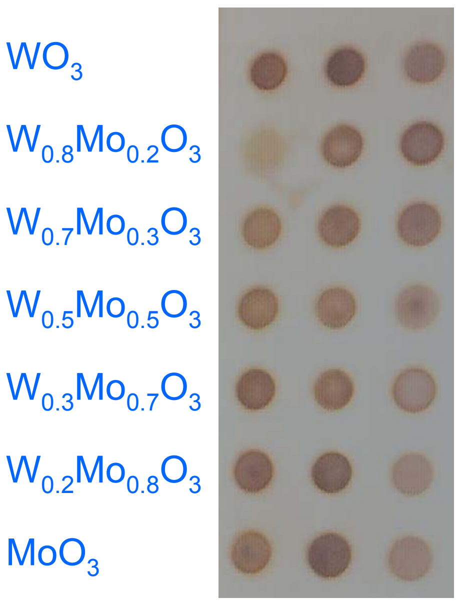


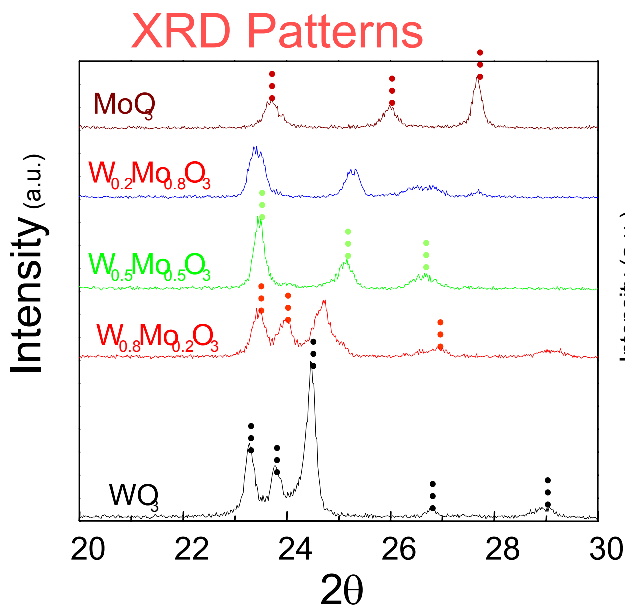
Pulse Voltage(V)
-1.0 -1.5 -2.0 -3.0
100% W
30% Pt / W
50% Pt / W
Pure Pt
Pure WO_3
Current Density(mA/cm^2)
Potential vs Pt reference(V)
Methanol Oxidation
Pure Pt
Current Density(mA/cm^2)
Potential vs Pt Electrode(V)
Potential vs Pt Electrode(V)
Potential vs Pt Electrode(V)

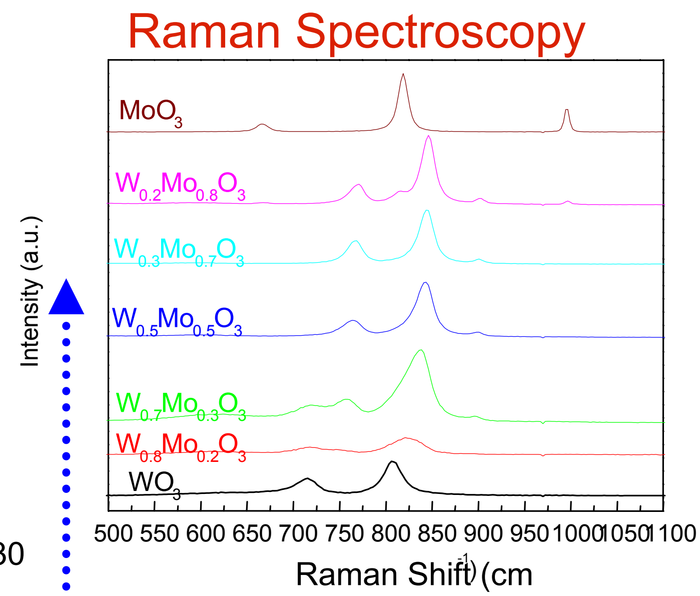
Tungsten-Molybdenum Mixed Oxides



- ✓ No prior reports of zerobias hydrogen evolution from WO_3 => Defect(doping) by electrodeposition shift flatband
- ✓ New, stable, substitutional phases discovered by electrodeposition and characterized
  - ❖ Superior photocatalytic oxidation properties
  - ❖ Significantly increased cation intercalation capacity.

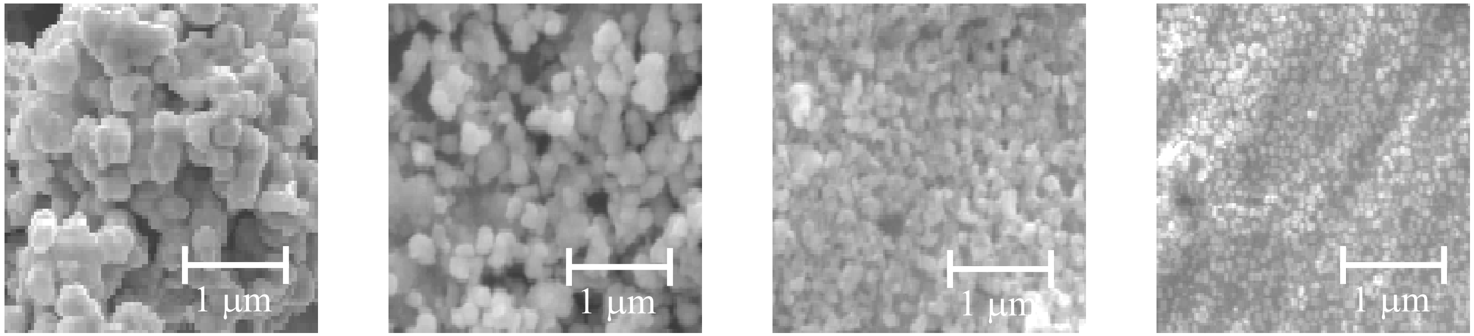




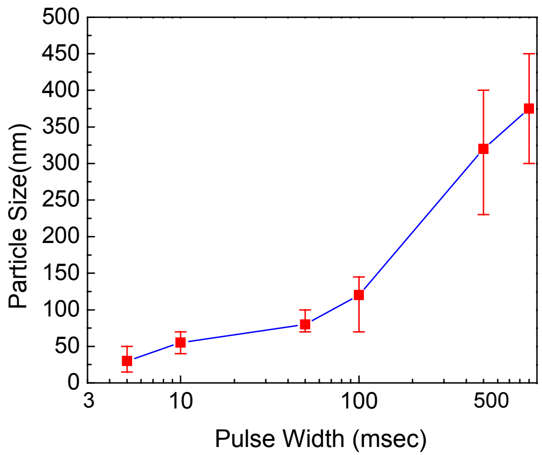


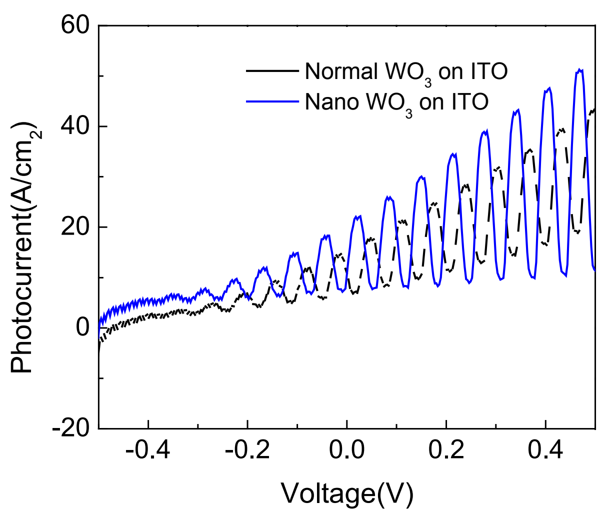
Increasing Mo Concentration

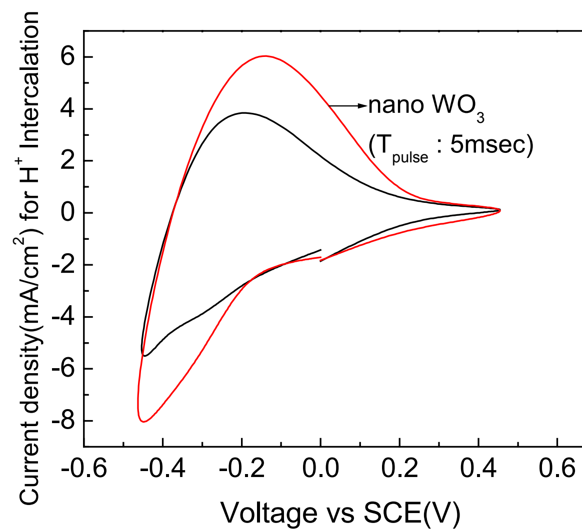
Electrodeposition of nanocrystalline WO_3 by pulsed deposition



T_{pulse} =500msec T_{pulse} =100msec T_{pulse} =50msec T_{pulse} =5msec





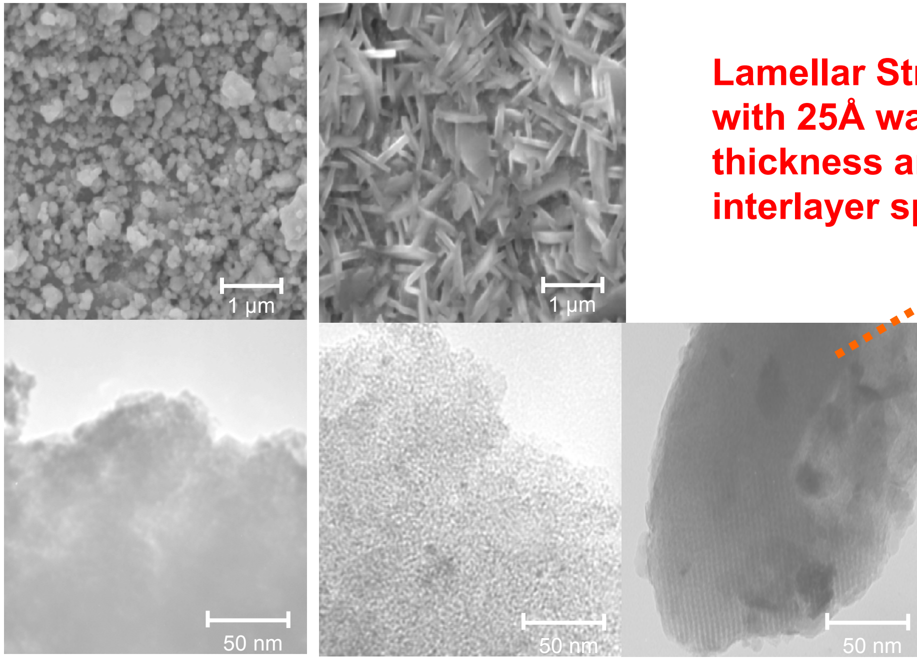


• S.H.Baeck, T. Jaramillo, G.D.Stucky, and E.W.McFarland,"Controlled Electrodeposition of Nanoparticulate Tungsten Oxide", **Nano Letters**, 2(8), 831(2002).

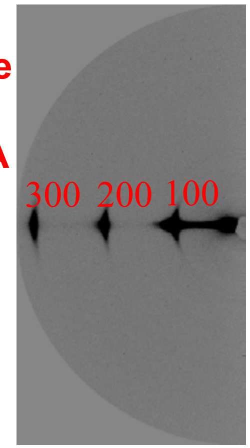
Electrodeposition of Mesoporous WO_3 Task: 7

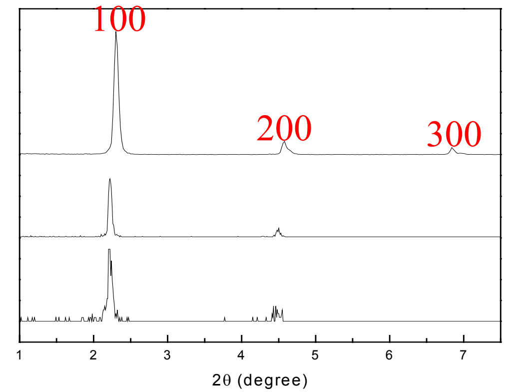
Accepted and in Pres *Adv. Materials* 2003

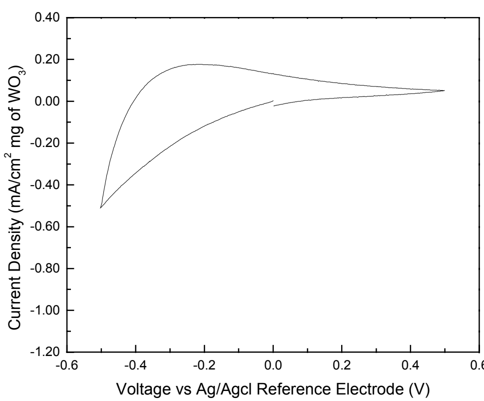
Nonporous Mesoporous

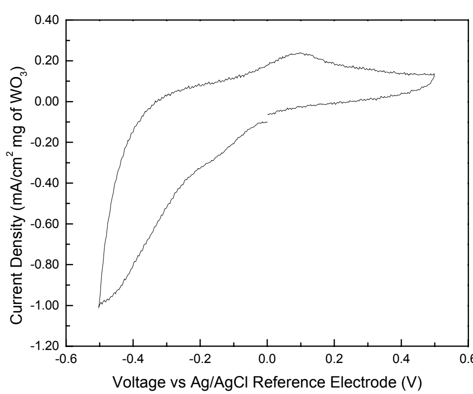


Lamellar Structure with 25Å wall thickness and 15Å interlayer spacing

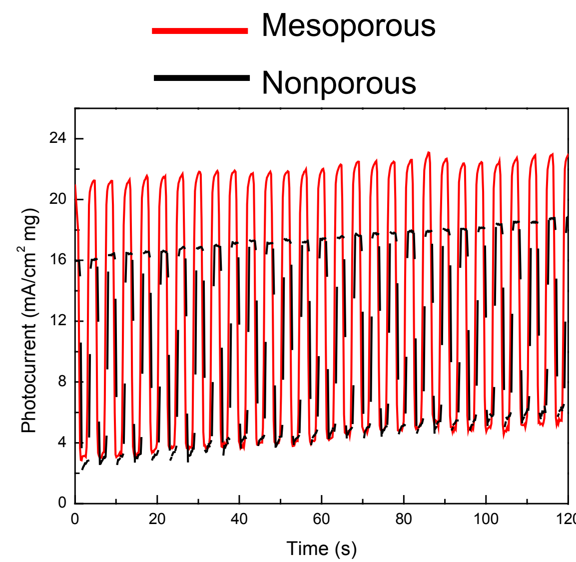






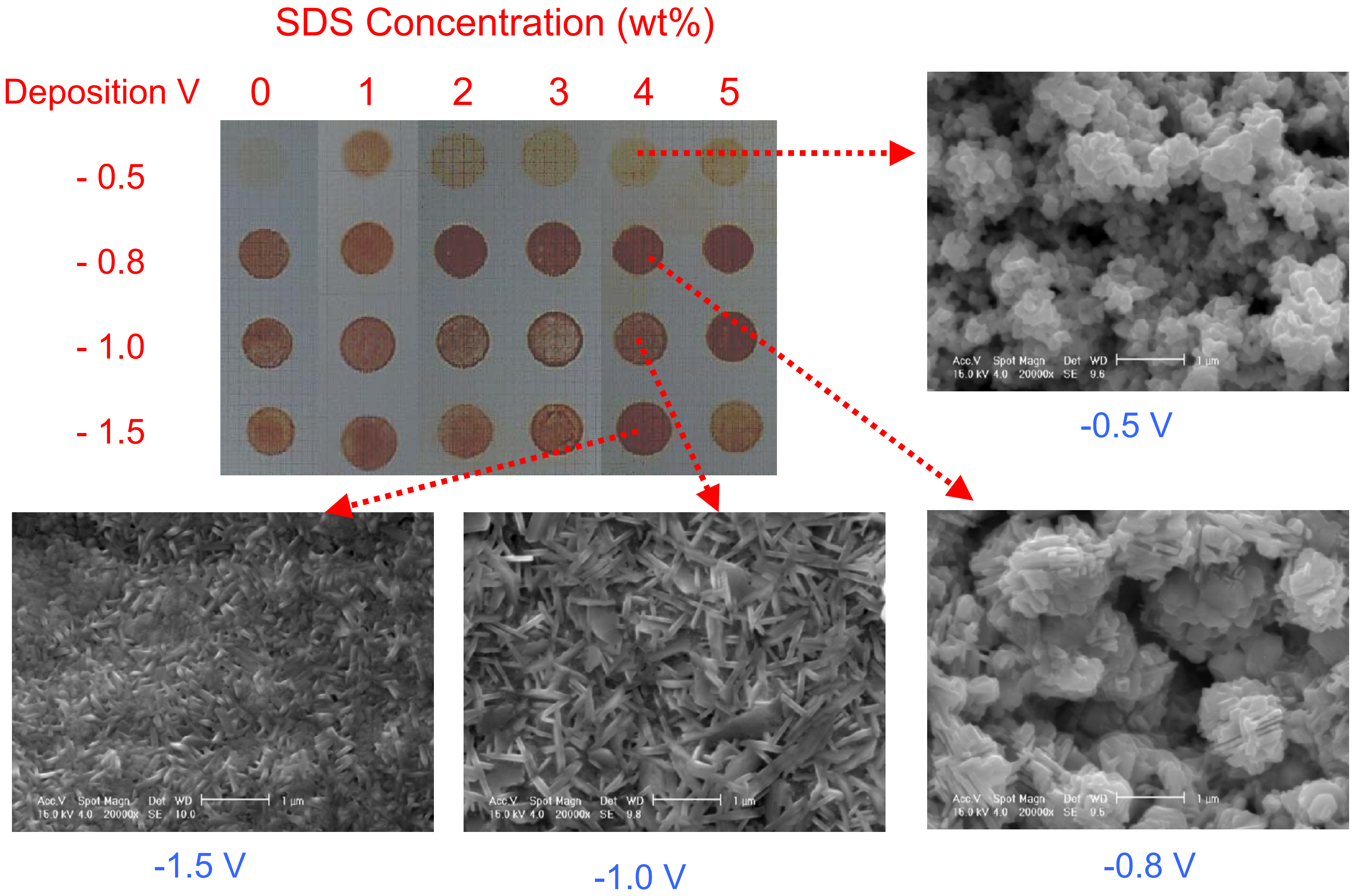


Hydrogen Intercalation

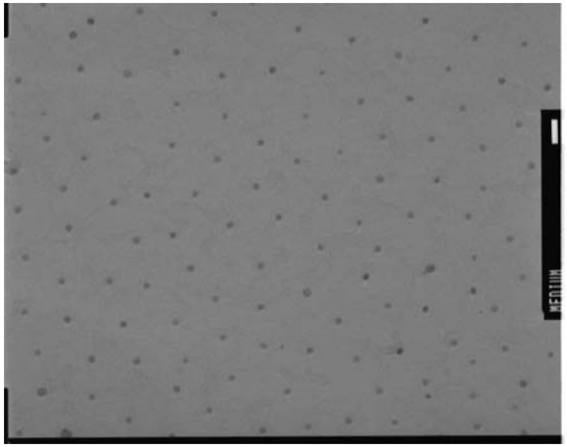


Zerobias Photocurrent

Mesoporous WO_3 Library with SDS

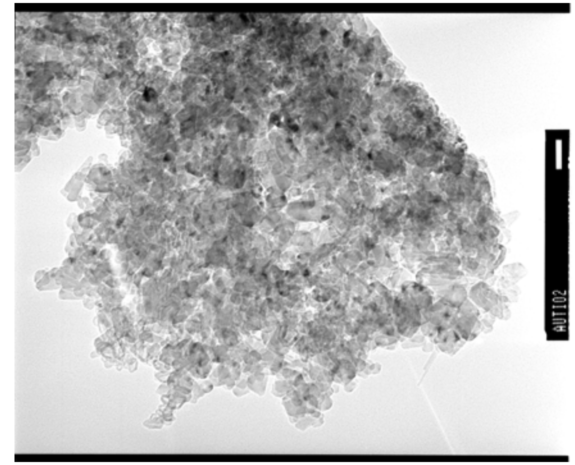


Block copolymer micelle encapsulation / Dip Coating



Thomas F. Jaramillo, S. H. Baeck, B. Roldan Cuenya, E.W.McFarland, *JACS* (2003) In Press

Electrodeposition of Nanoparticles

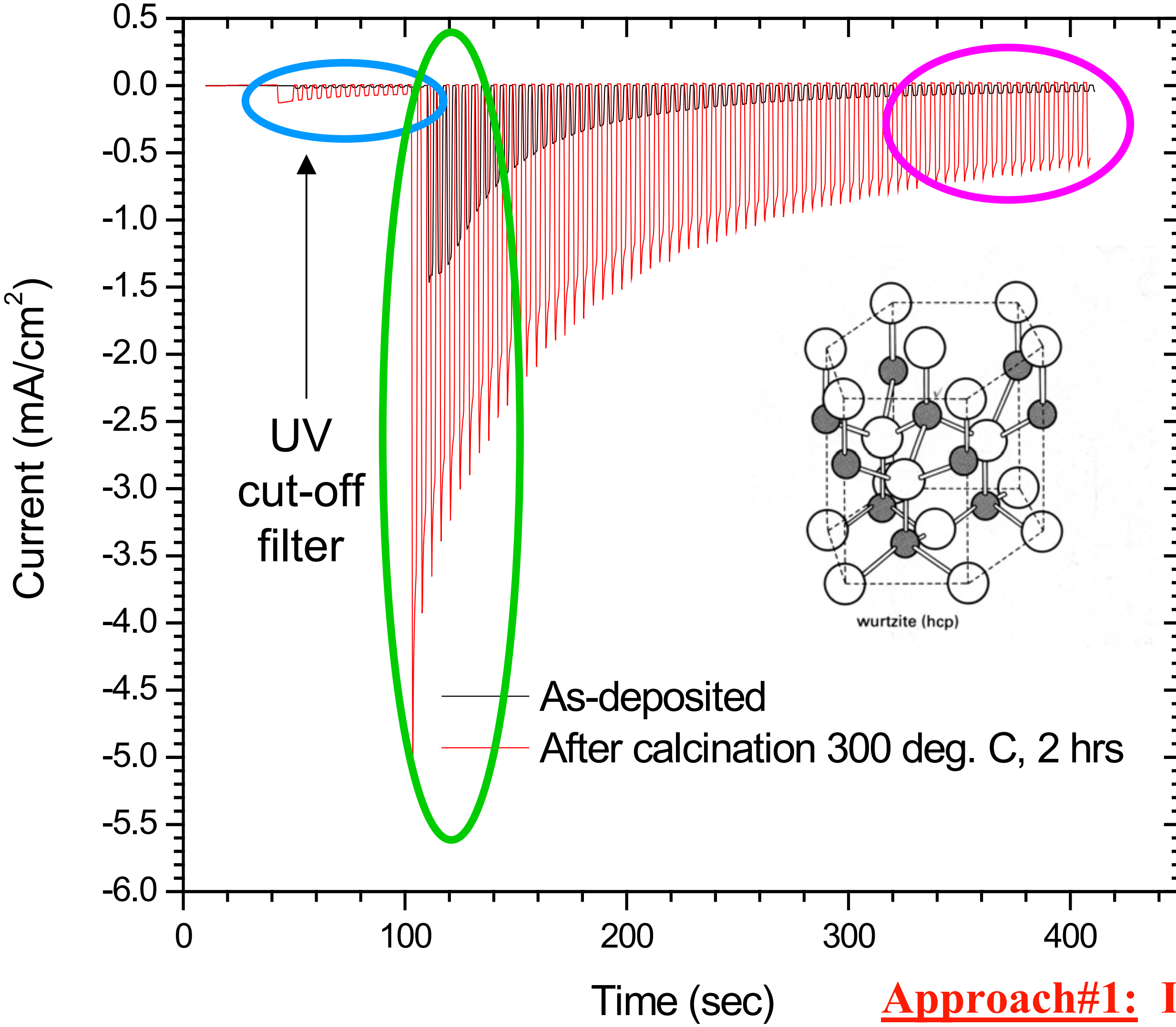


S. H. Baeck, Thomas F. Jaramillo, E.W.McFarland, *Proc. ACS* (2003)

	Block copolymer micelle encapsulation / Dip Coating	Electrodeposition of Nanoparticles
Advantage	• Uniform Dispersion • Narrow Particle size distribution • Particle size & Density can be controlled by template	• Electrically active by design • No requirement of post treatment • Particle size & Density can be controlled by deposition condition
Disadvantage	• Post treatment (Removal of Polymer) • Doping density limitation (monolayer)	• Broad particle size distribution • Non-uniform Dispersion

Task 2: Zinc Oxide Photocatalyst Host

Inexpensive in bulk
High conductivity
High Dopant Solubility



Promising
Photocatalytically active (in the UV)

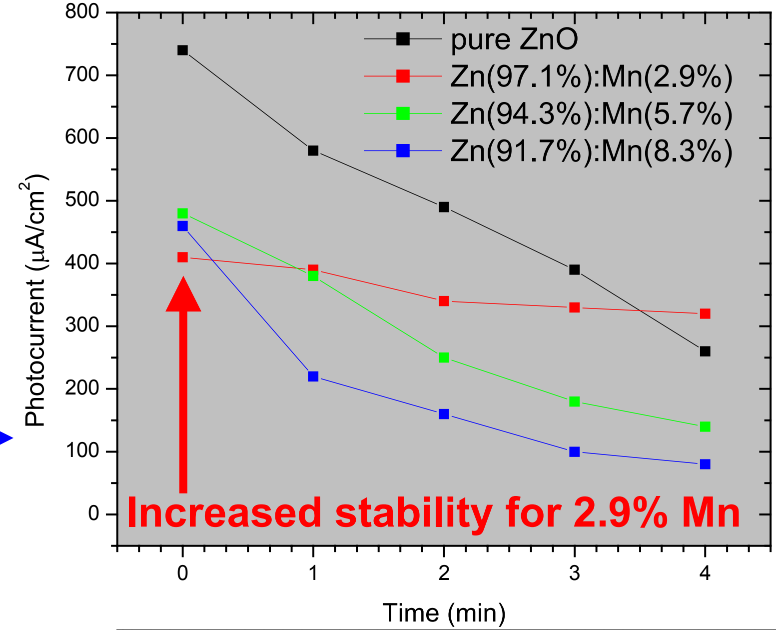
Unfortunate
3 eV Bandgap, minimal visible light photocurrent

Unacceptable
Photocurrent decay from photoanodic corrosion

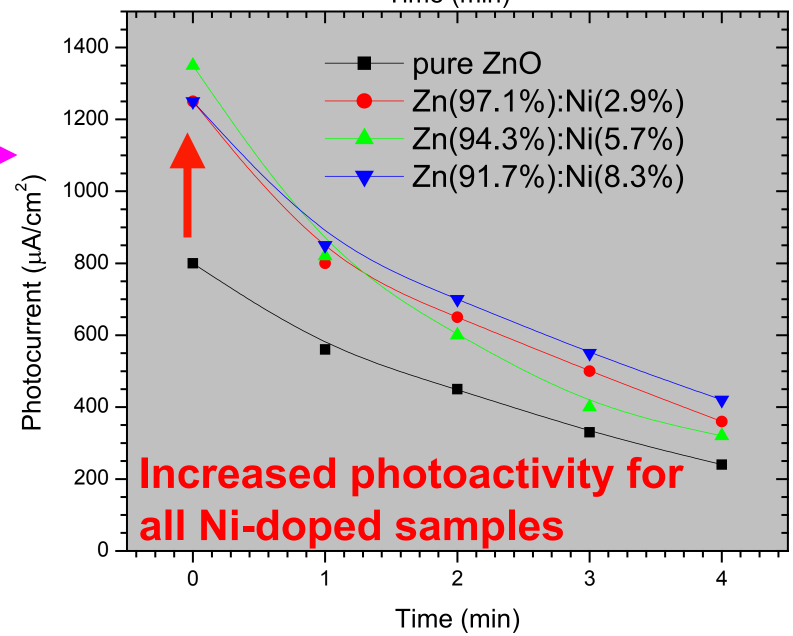
Approach#1: Introduce dopants to improve visible absorption

Other Transition metal doped ZnO library: Fe, Cr, Mn, Ni

		A	B	C	D
$Fe(NO_3)_2$	1	0%	0.6%	1.0%	1.5%
$CrCl_3$	2	0%	2.9%	5.7%	8.3%
$MnCl_2$	3	0%	2.9%	5.7%	8.3%
$NiCl_2$	4	0%	2.9%	5.7%	8.3%



All depositions:
200mM $Zn(NO_3)_2$ in DMSO (no saturated O_2)
except Fe row (100mM $ZnCl_2$)
-1.16V vs. Ag pseudo-reference (-1.0 vs. Ag/AgCl)
85 deg. C
15min deposition onto ITO-coated glass substrate



Mn improves ZnO stability.
Ni improves ZnO photoactivity in the UV
Fe may increase photoactivity in the visible
To date best is Co which improves both.

Communication and Cooperative Efforts: Task 8

Internal:

Strong collaborations with the laboratory of Professor Galen Stucky and UCSB Materials Research Laboratory (NSF)

External:

Frequent academic and industrial presentations.

Participant in the IEA Hydrogen Production Task Committee.

Cooperation with SBA Materials, Inc. and the Cycad Group, Inc. exploring issues related to process economics for commercialization of photoelectrocatalysis and photoelectroxidation. Licensing of Patents.

Publications Resulting from DOE Hydrogen Program Funding (Sept. 01-Present):

1) "High-Throughput Screening System for Catalytic Hydrogen-Producing Materials," *J. Combinatorial Chem.* 4 (1) 17-22 (2002).
2) "Combinatorial Electrochemical Synthesis and Characterization of Tungsten-Molybdenum Mixed Oxides," *Korean J. Chem. Engin.* 19 (4) 593-596 (2002).
3) "Combinatorial Electrochemical Synthesis and Characterization of Tungsten-based Mixed Metal Oxides," *J. Combi. Chem.* Vol 4(6) 563-568 (2002).
4) "Controlled Electrodeposition of Nanoparticulate Tungsten Oxide," *Nanoletters* 2 (8) 831-834 (2002).
5) "Influence of Composition and Morphology on Photo and Electrocatalytic Activity of Electrodeposited Pt/WO3," *Am.Chem.Soc., Abs.Pap. 224: 062-FUEL Part 1* (2002)
6) "Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials," (2002) *Proceedings of the 2002, DOE Hydrogen Program Review* NREL/CP-610-32405
7) "A Cu2O/TiO2 Heterojunction Thin Film Cathode for Photoelectrocatalysis," *Solar Energy Materials.* Vol. 77, 3,229-237 (2003).
8) "Electrochemical Synthesis of Nanostructured ZnO films Utilizing Self Assembly of Surfactant Molecules at Solid-Liquid Interfaces," *J. Am. Chem. Soc.* 124(42); 12402-12403 (2002)
9) "Electrocatalytic Properties of Thin Mesoporous Platinum Films Synthesized Utilizing Potential-Controlled Surfactant Assembly," *Advanced Materials.* (Accepted and in press 2003).
10) "Catalytic Activity of Supported Au Nanoparticles Deposited From Block Co-polymer Micelles", (Accepted and in Press 2003, *J. Am. Chem. Soc.*)
11) "Enhancement of Photocatalytic and Electrochromic Properties of Electrochemically Fabricated Mesoporous WO3 Thin Films", Submitted Adv. Materials 2003
12) "Synthesis of Tungsten Oxide on Copper Surfaces by Electroless Deposition" Submitted Chem. Mater. (2003).

Education:

Students - Tom Jaramillo, Anna Ivanovskaya, Alan Kleinman

Post-Doctoral Associates – Dr. Sung-Hyeon Baeck, Dr. Kyoung-Shin Choi

Visiting Scholars – Professor Withana Siripala