Liquid Sunlight Alliance

Harry A. Atwater | DIRECTOR

BESAC Meeting
July 27th, 2023

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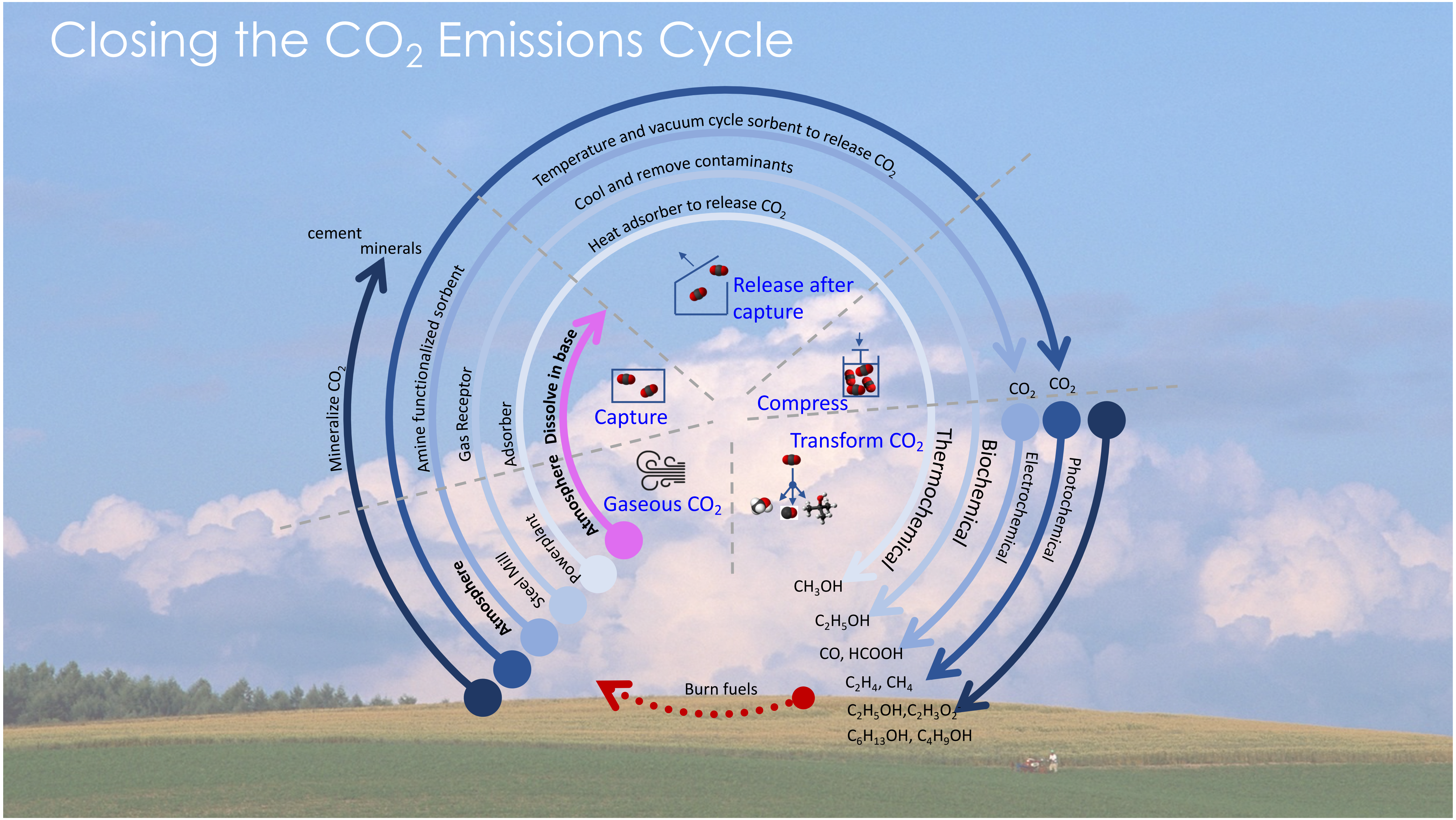
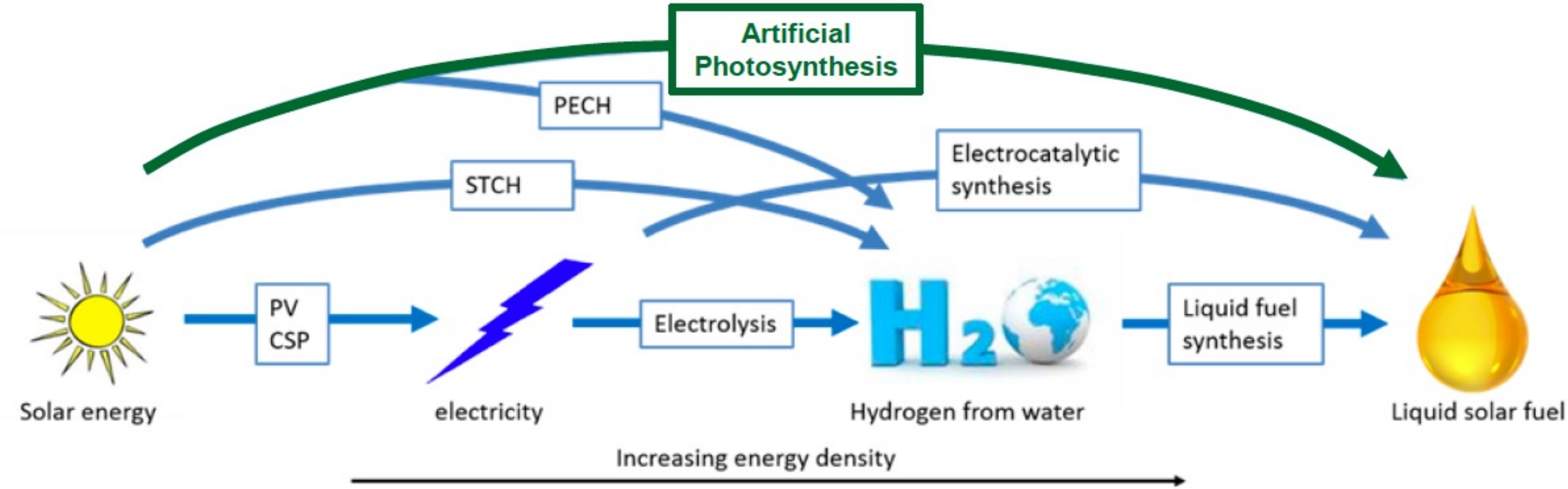


Closing the CO_2 Emissions Cycle
Temperature and vacuum cycle sorbent to release CO_2
Cool and remove contaminants
Heat adsorber to release CO_2
cement
minerals
Mineralize CO_2
Amine functionalized sorbent
Gas Receptor
Adsorber
Dissolve in base
Atmosphere
Powerplant
Steel Mill
Atmosphere
Release after capture
Capture
Compress
Gaseous CO_2
Transform CO_2
CO_2
CO_2
Thermochemical
Biochemical
Electrochemical
Photochemical
CH_3OH
C_2H_5OH
CO, HCOOH
C_2H_4, CH_4
C_2H_5OH, $C_2H_3O_2^-$
$C_6H_{13}OH$, C_4H_9OH
Burn fuels

Direct solar to liquid fuels via artificial photosynthesis



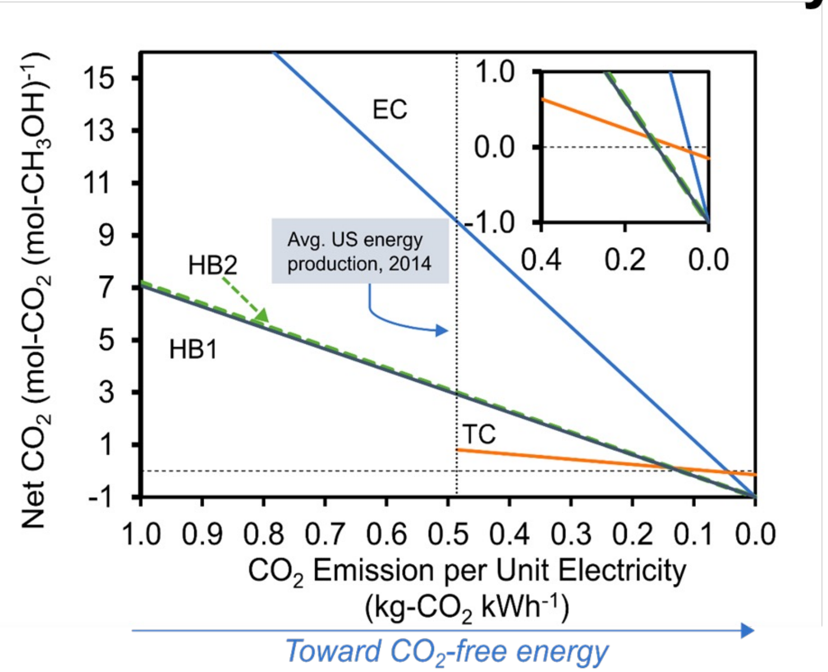
Is there a need for solar fuels?

Yes.

Carbon intensity of fuels formed by grid electrolysis will be carbon-positive until >2050, because grid will not be 100% green.

Tackett, Gomez & Chen, *Nature Catalysis*, 2 (2019) 381

CO_2 Mass Balance for Methanol Synthesis



TC: Thermocatalytic conversion of CO_2 to CH_3OH
EC: Electrocatalytic conversion of CO_2 to CH_3OH
HB1: CO_2-free H_2 from electrolysis for thermocatalysis of CO_2 to CH_3OH
HB2: Electroreduction of CO_2 to ($CO + H_2$) for thermal CH_3OH synthesis

Liquid Sunlight Alliance

https://www.liquidsunlightalliance.org

Vision: Establish science principles by which coupled microenvironments directly generate liquid fuels from sunlight, water, carbon dioxide and nitrogen.

- Unprecedented catalytic selectivity, durability, and efficiency
- pure and impure feedstocks; fluctuating solar resource

Strategy:

Create coupled microenvironments by co-design

Team:

Caltech BERKELEY LAB NREL NATIONAL RENEWABLE ENERGY LABORATORY SLAC
UCI University of California, Irvine | UNIVERSITY OF OREGON | UC San Diego

Transformative Impacts and Outcomes:

- A new 'co-design of microenvironments' science paradigm for generation of liquid solar fuels with unprecedented selectivity, durability, and efficiency
- The science foundations for direct solar-driven synthesis of multi-carbon products from mixed and dilute CO_2 feedstocks
- Discovery of innovative light-driven phenomena in chemically complex environments
- A new predictive science of materials durability and active repair in electrochemical systems
- A national alliance for solar fuels science spanning academic, national labs and industry sectors, creating a platform for next-generation solar fuels technologies

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Artificial photosynthesis, at almost 50 years old, is still in its infancy

Dr. Kenichi Honda (Japan) Dr. Akira Fujishima (Japan)

Electrochemical Photolysis of Water at a Semiconductor Electrode

ALTHOUGH the possibility of water photolysis has been investigated by many workers, a useful method has only now been developed. Because water is transparent to visible light it

AKIRA FUJISHIMA

Department of Applied Chemistry, Kanagawa University, Yokohama

KENICHI HONDA

Institute of Industrial Science, University of Tokyo, Roppongi, Tokyo

Received September 13, 1971; final revision April 24, 1972.

NATURE VOL. 238 JULY 7 1972

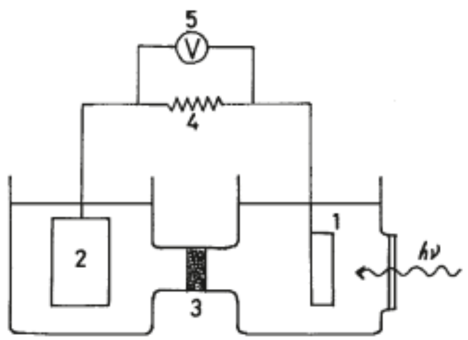


Fig. 2 Electrochemical cell in which the TiO_2 electrode is connected with a platinum electrode (see text). The surface area of the platinum black electrode used was approximately 30 cm².

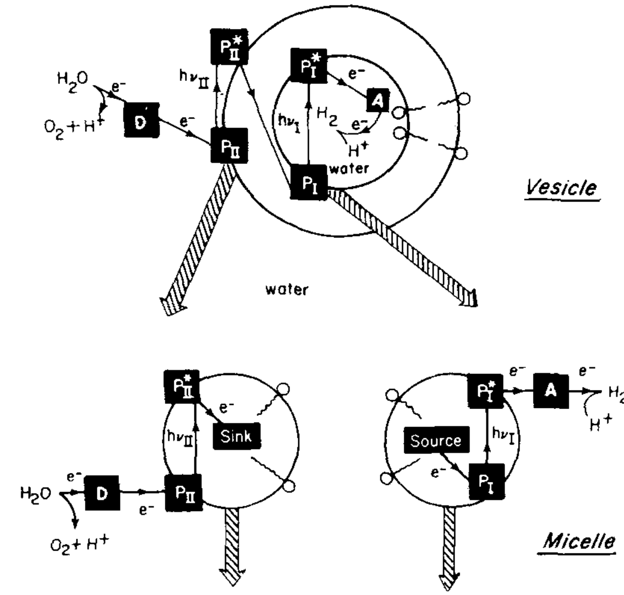
ARTIFICIAL PHOTOSYNTHESIS: QUANTUM CAPTURE AND ENERGY STORAGE

MELVIN CALVIN

Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, USA

(*Received* 16 *August* 1982; *accepted* 4 *October* 1982)

Abstract—Organized systems are described to achieve separation of the charges produced by quantum absorption in a sensitizer, and their stabilization in separated chemical form. These systems involve phase boundary charge separation by both membranes and charged particles, in both cases simulating the natural system.



Solar fuels to date has focused on photocatalysis at individual reaction centers

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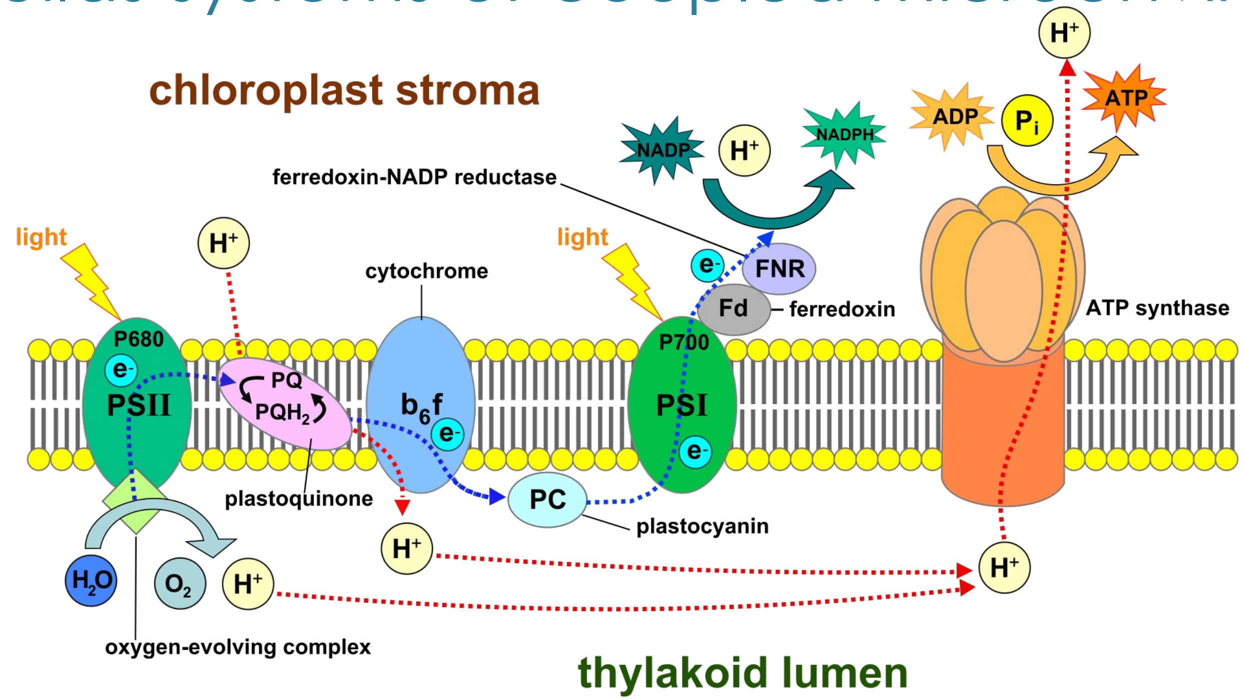
But nature builds systems of coupled microenvironments



Light dependent reaction: 2 H_2O + 2 $NADP^+$ + 3 ADP + 3 P_i + light → 2 NADPH + 2 H^+ + 3 ATP + O_2

Calvin cycle: 3 CO_2 + 9 ATP + 6 NADPH + 6 H^+ → $C_3H_6O_3$-phosphate + 9 ADP + 8 P_i + 6 $NADP^+$ + 3 H_2O

Microenvironments in photosynthesis are at once highly integrated but compartmentalized

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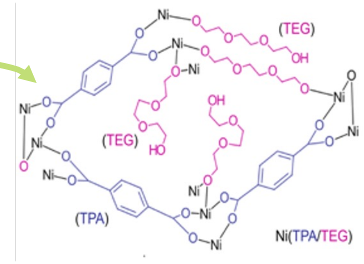
Two paths for liquid fuels via artificial photosynthesis

- Design single reaction center:

CO_2 →



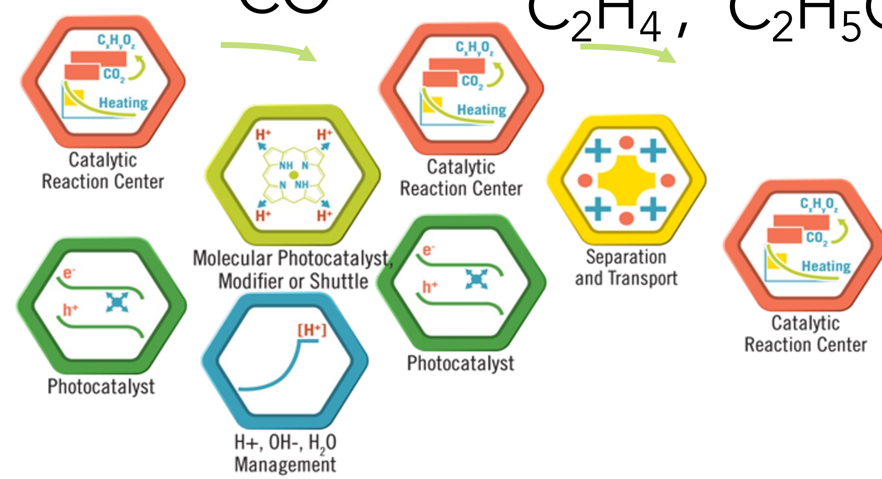
→ CO

CH_3OH..

C_2H_5OH?

- Coupled microenvironments:

CO_2 → CO → C_2H_4 , C_2H_5OH → $C_{5\text{-}10}$



Coupling microenvironments opens many directions for liquid solar fuels

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Liquid Sunlight Alliance

Management Team


Harry Atwater
Director
Caltech


Frances Houle
Deputy Director
LBNL


Bill Tumas
Community Alliance Coordinator NREL

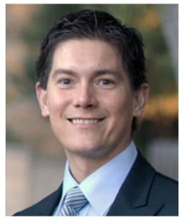

Tom Jaramillo
Science Impacts Coordinator SLAC


Carrie Hofmann
Associate Director,
Caltech

Team Leads


John Gregoire
Photoactive Materials
Caltech


Junko Yano
Photodynamics
LBNL

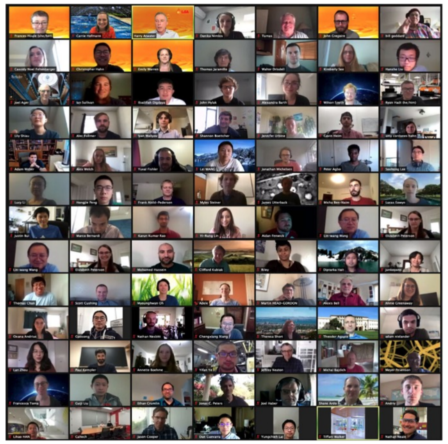

Tom Jaramillo
Durability
SLAC


Theo Agapie
Chemical μenvironments
Caltech


Emily Warren
Systems and Integration NREL


Walter Drisdell
User Facilities Lead LBNL

- 38 PIs & > 120 researchers



- Began completely remote in 2020…
- Transitioned to in-person in 2022-23

Diverse expertise in solar fuels, inorganic chemistry, accelerated materials discovery, *operando* measurement, materials & catalysis theory and experiments, systems design

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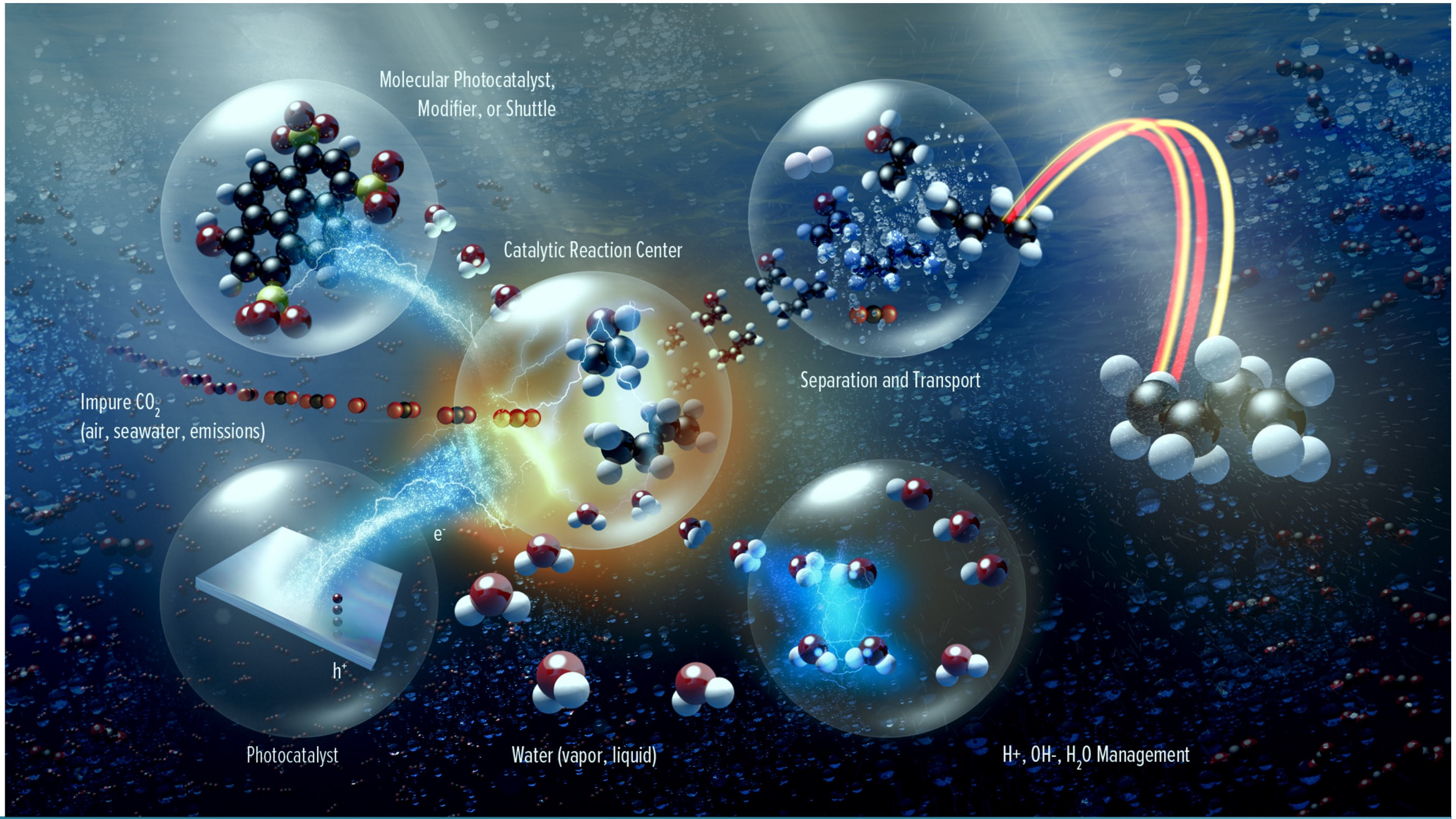
LiSA's Goals

Goal 1: Understand and integrate multi-component systems of coupled microenvironments , tailoring molecules and materials for achieving targeted functionality in transport and activity around the active site.



Goal 1: Realize multicomponent systems comprised of coupled microenvironments

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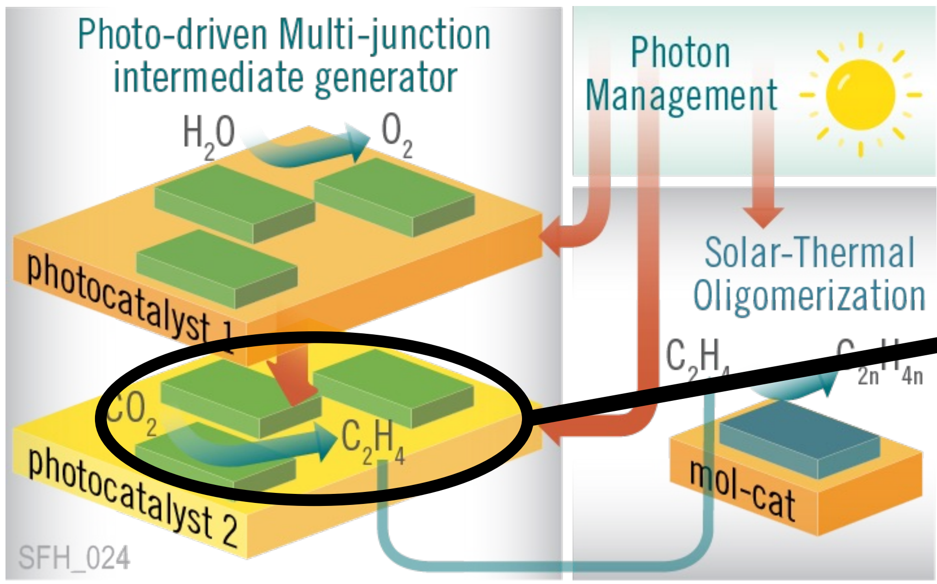
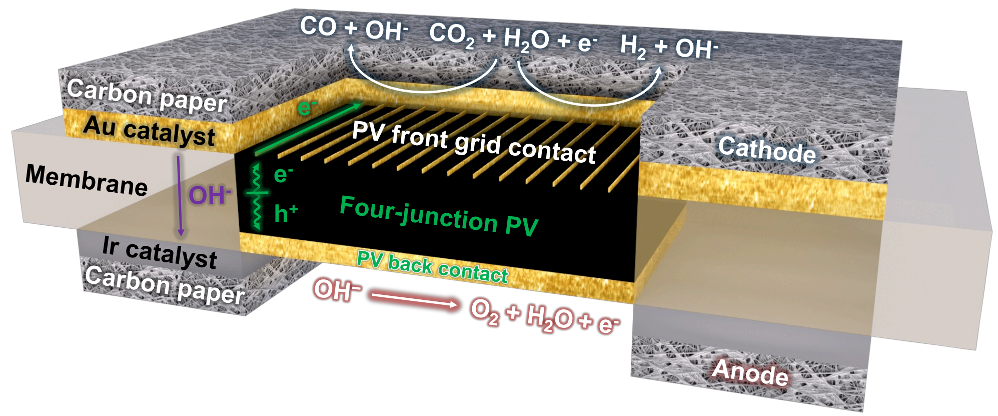
1

GOAL

Design of hierarchical assemblies to produce solar liquid fuels





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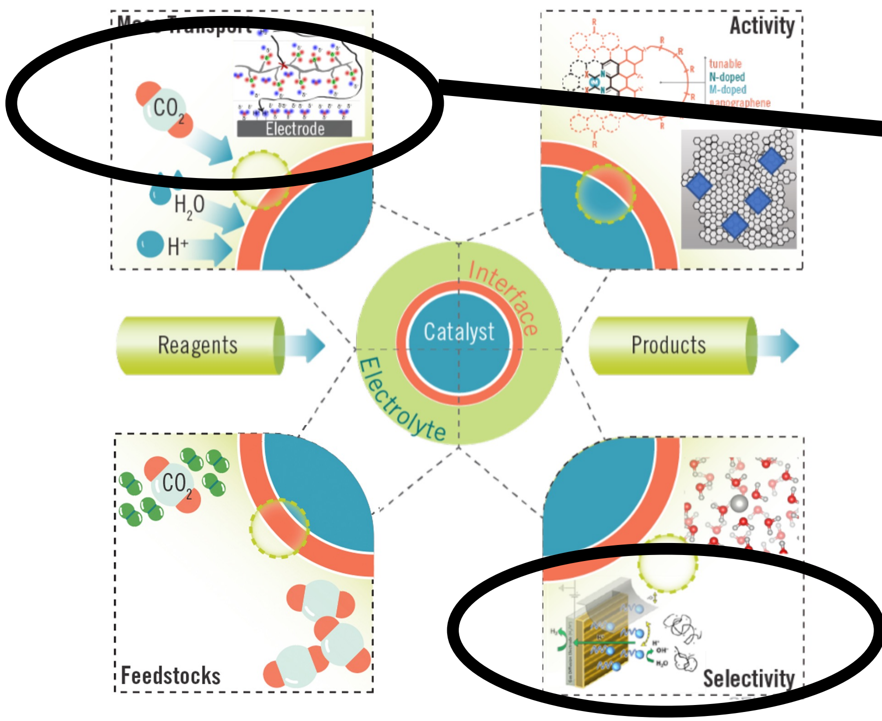
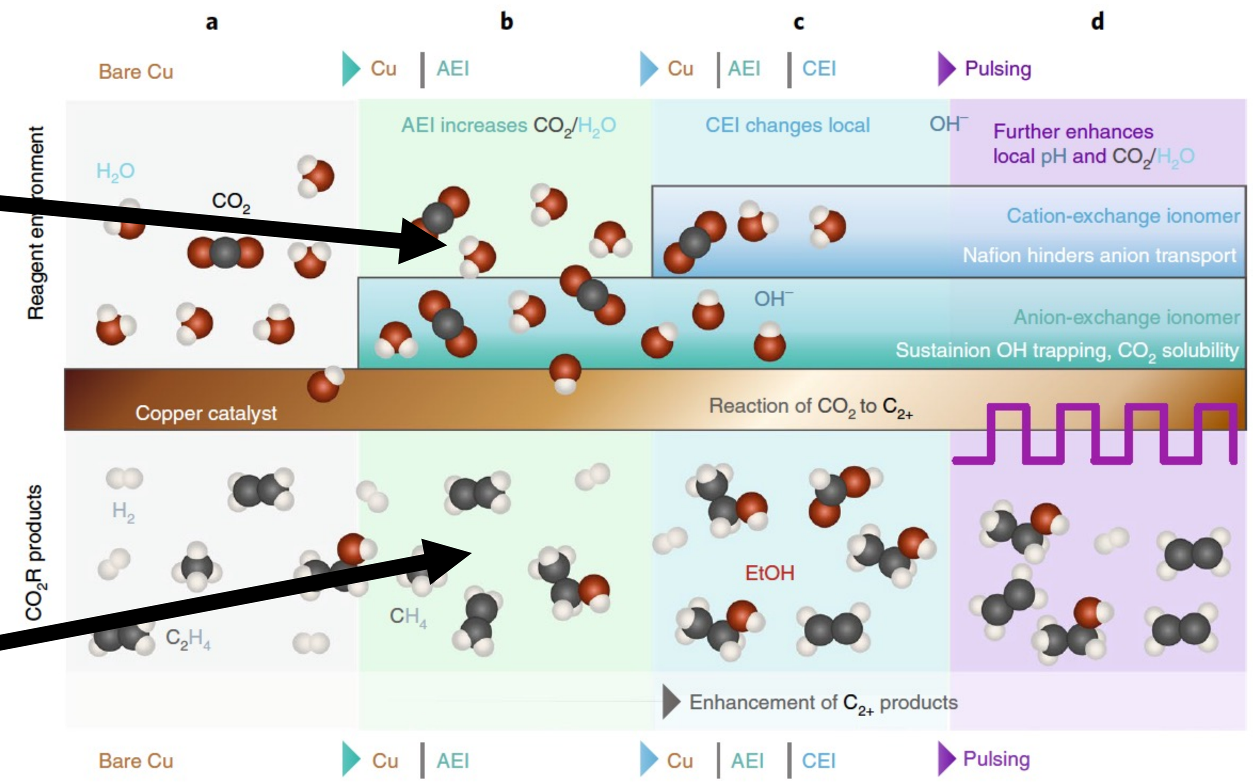
1

GOAL

Tailoring molecules and materials for targeted functionality





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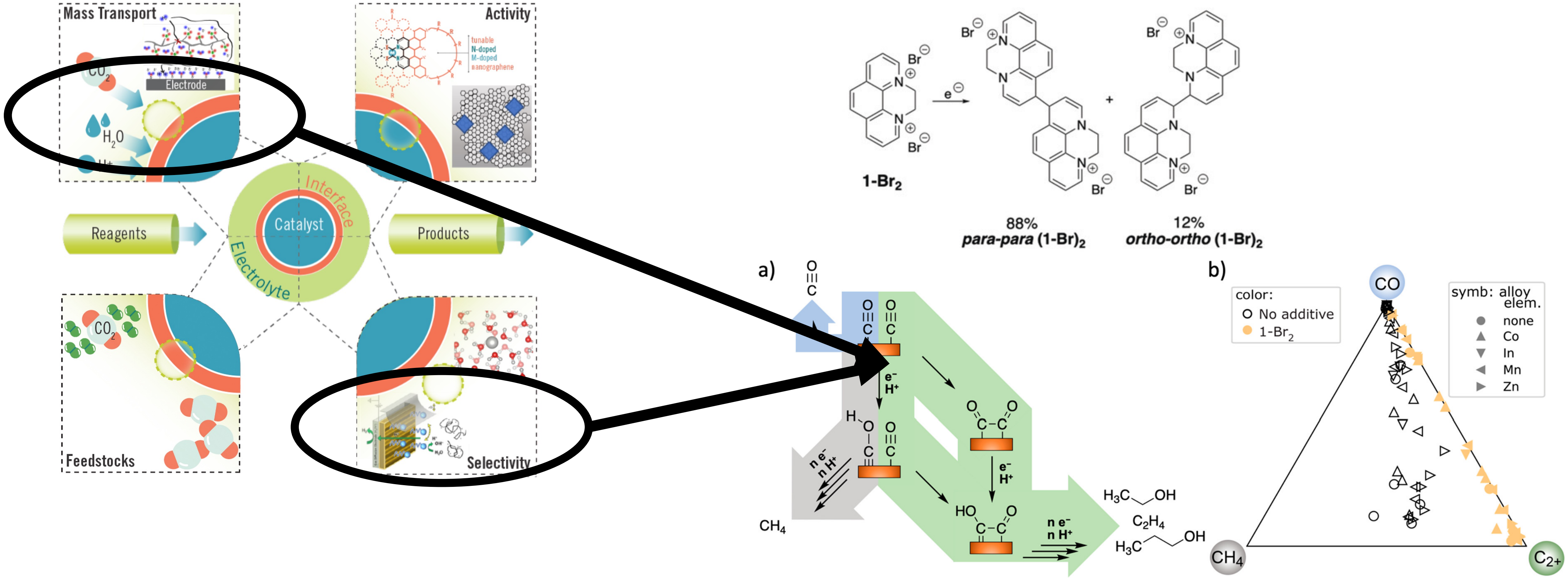
1
GOAL

Tailoring molecules and materials for targeted functionality



1
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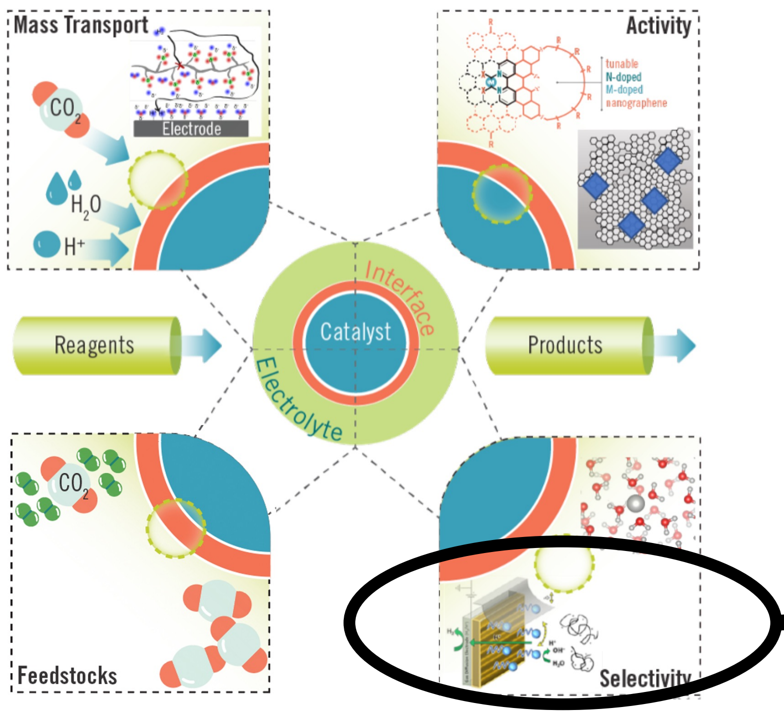
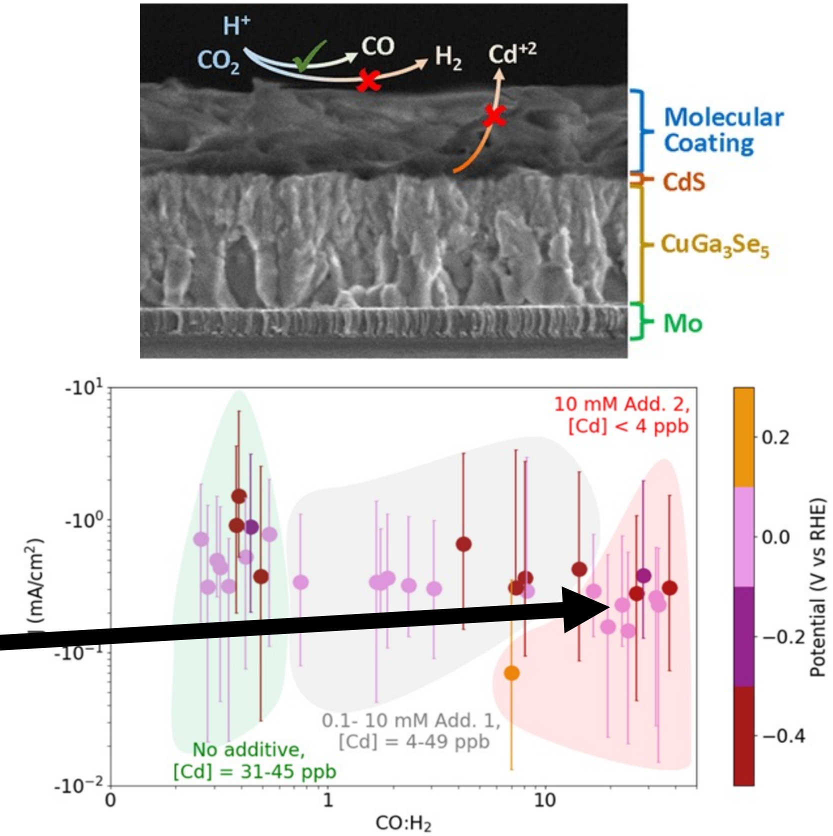
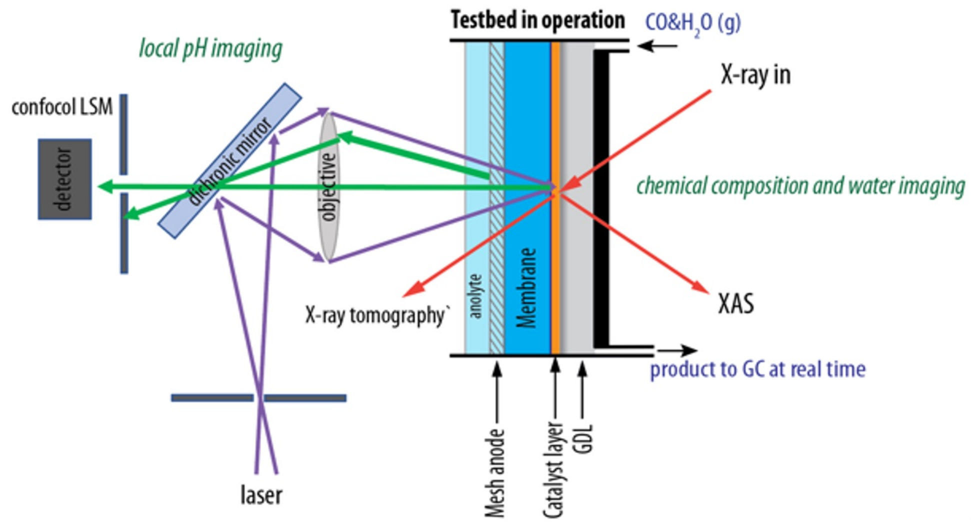
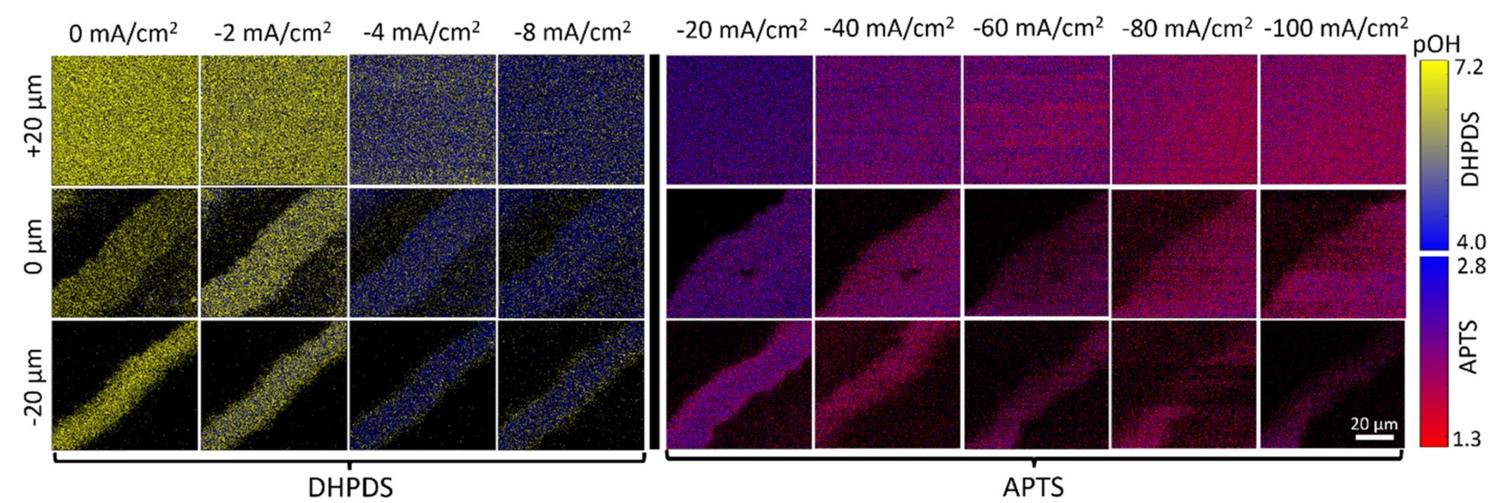




1
GOAL

Design of hierarchical assemblies to produce solar liquid fuels





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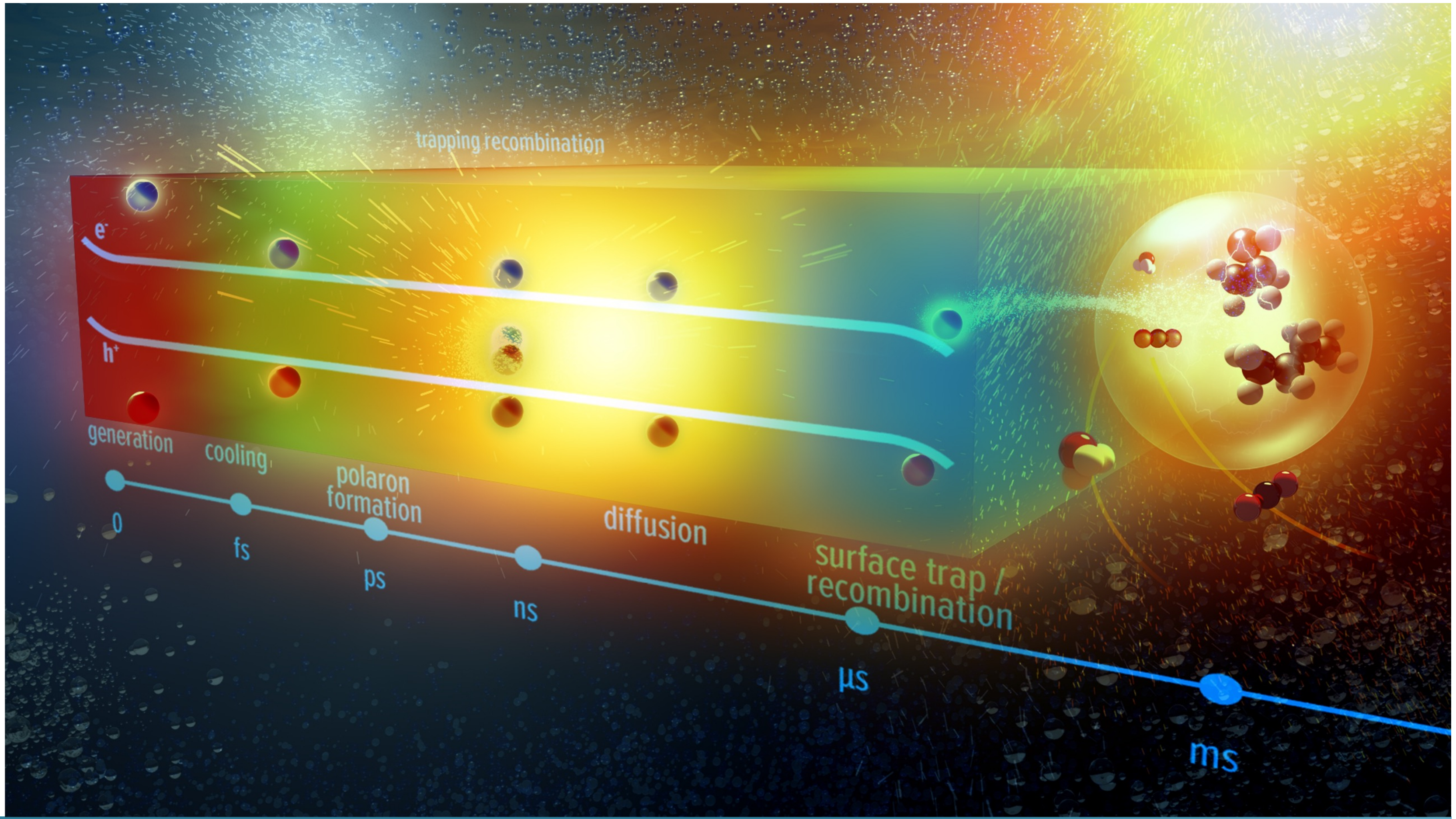
LiSA's Goals

Goal 2: Discover photon, electron, and molecular processes, from light excitation to the catalytic center: realizing ensembles of molecules and materials that achieve efficiency and selectivity beyond those available with conventional electrochemical processes.



Goal 2: Discover and harness photodynamics from excitation to the catalytic center

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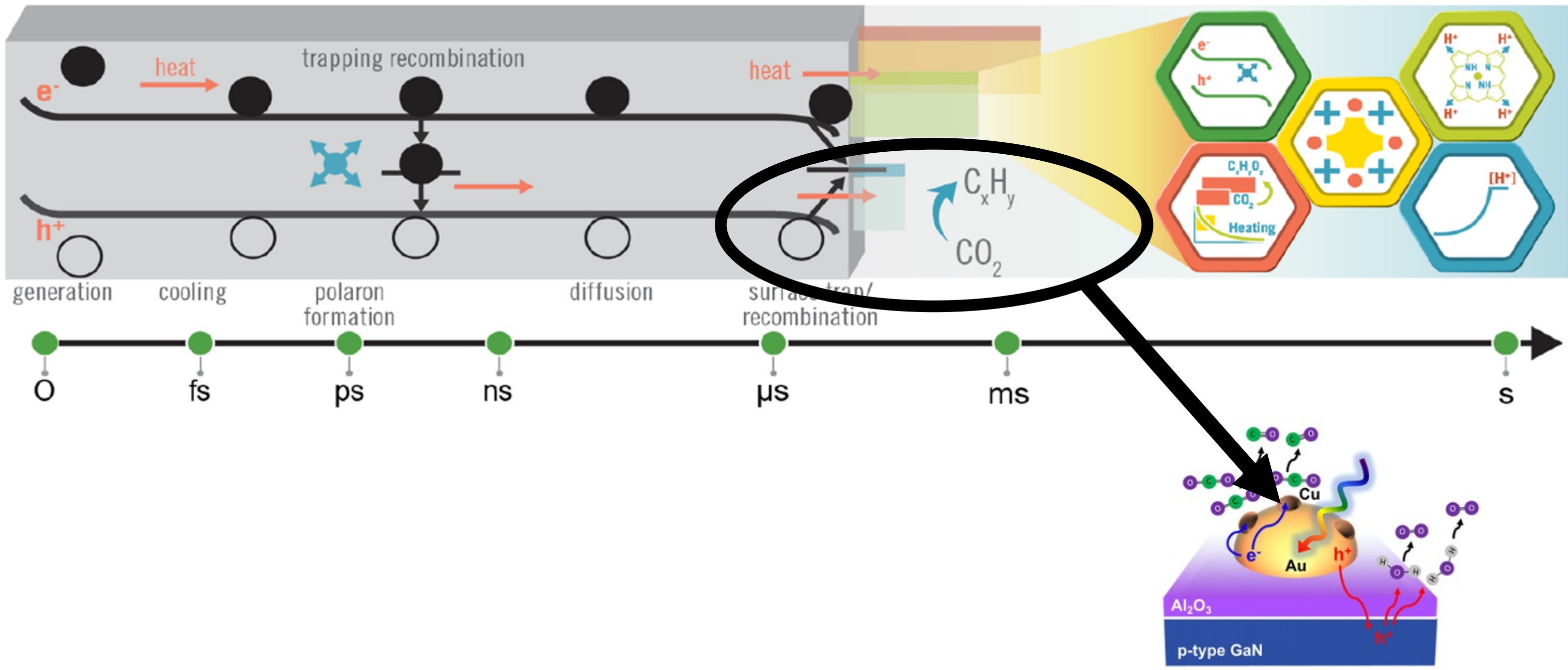
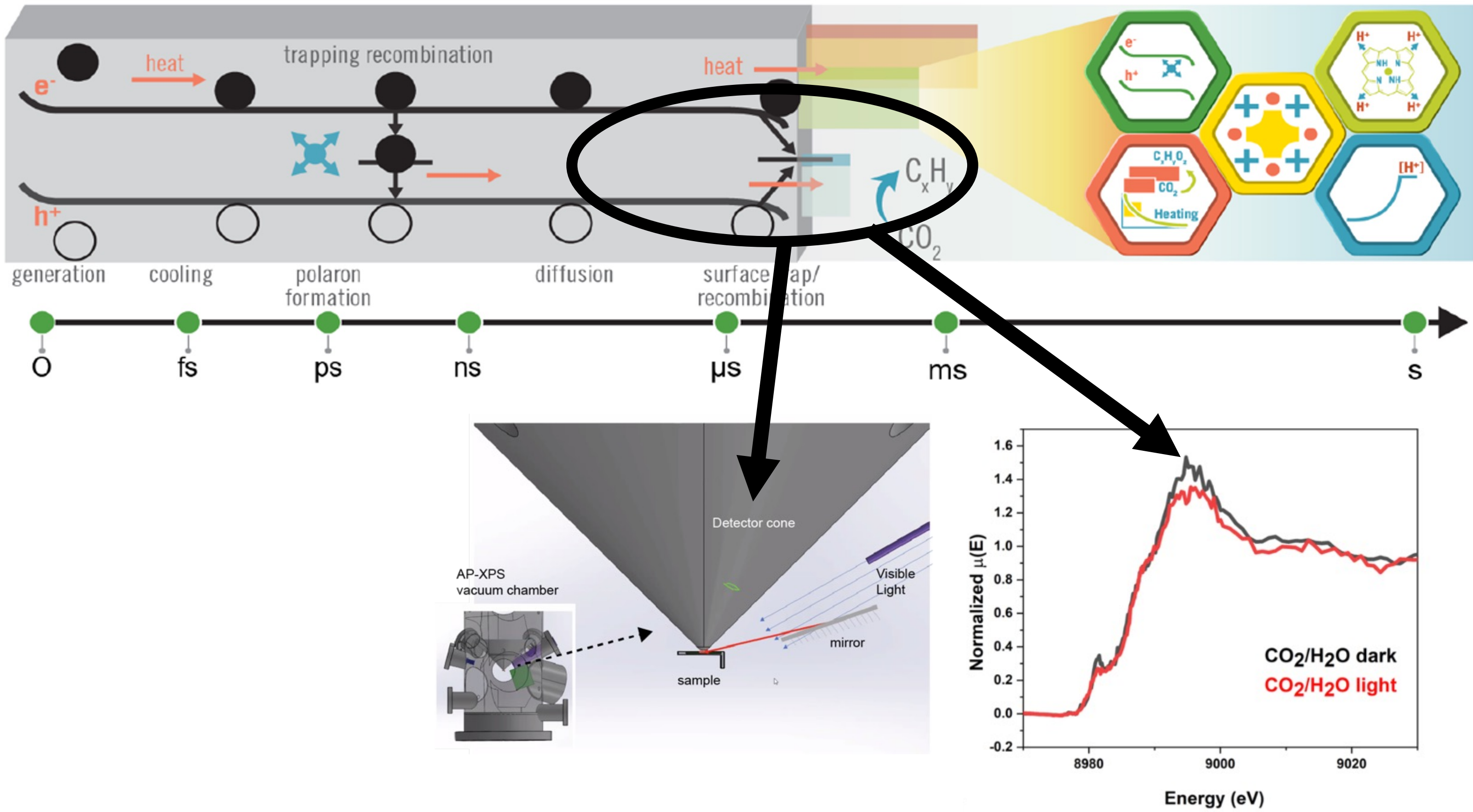
2 GOAL Photon, electron, and molecular processes from excitation to catalytic center



2 GOAL

Photon, electron, and molecular processes from excitation to catalytic center



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2
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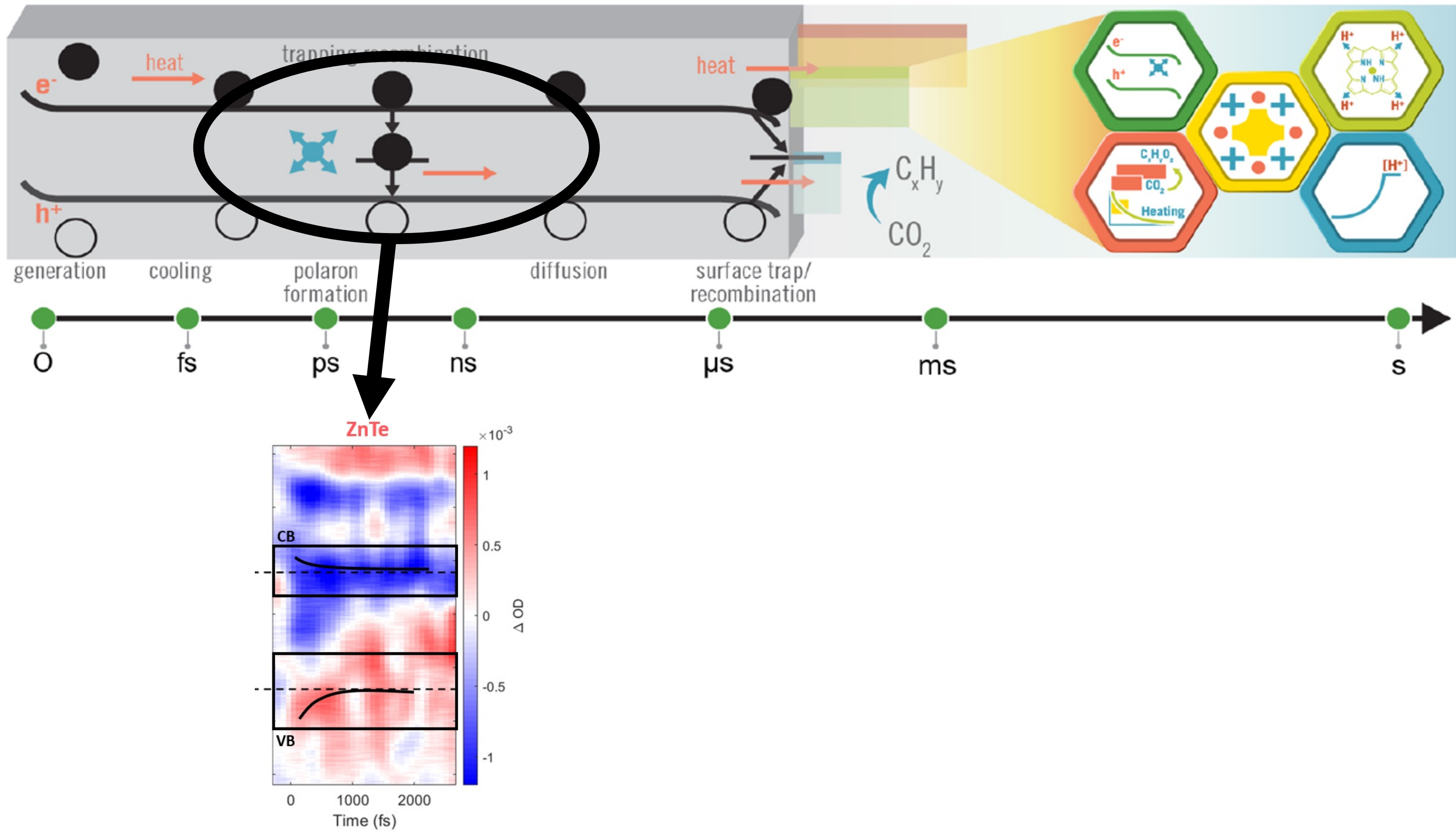
Photon, electron, and molecular processes from excitation to catalytic center



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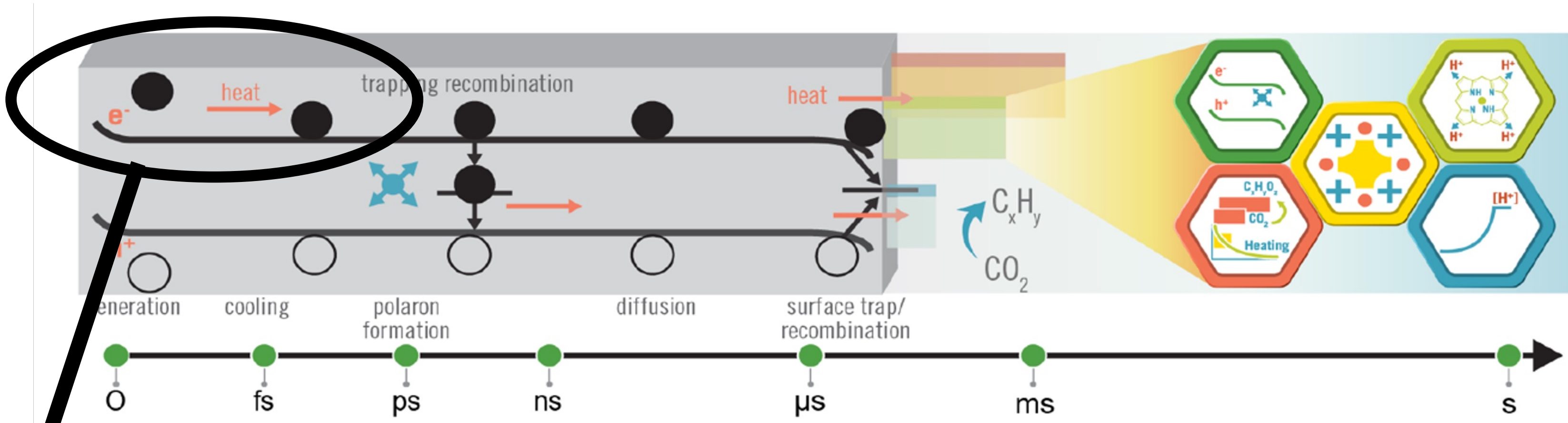
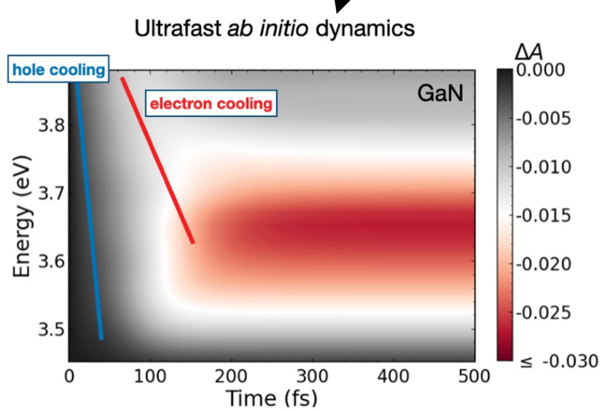
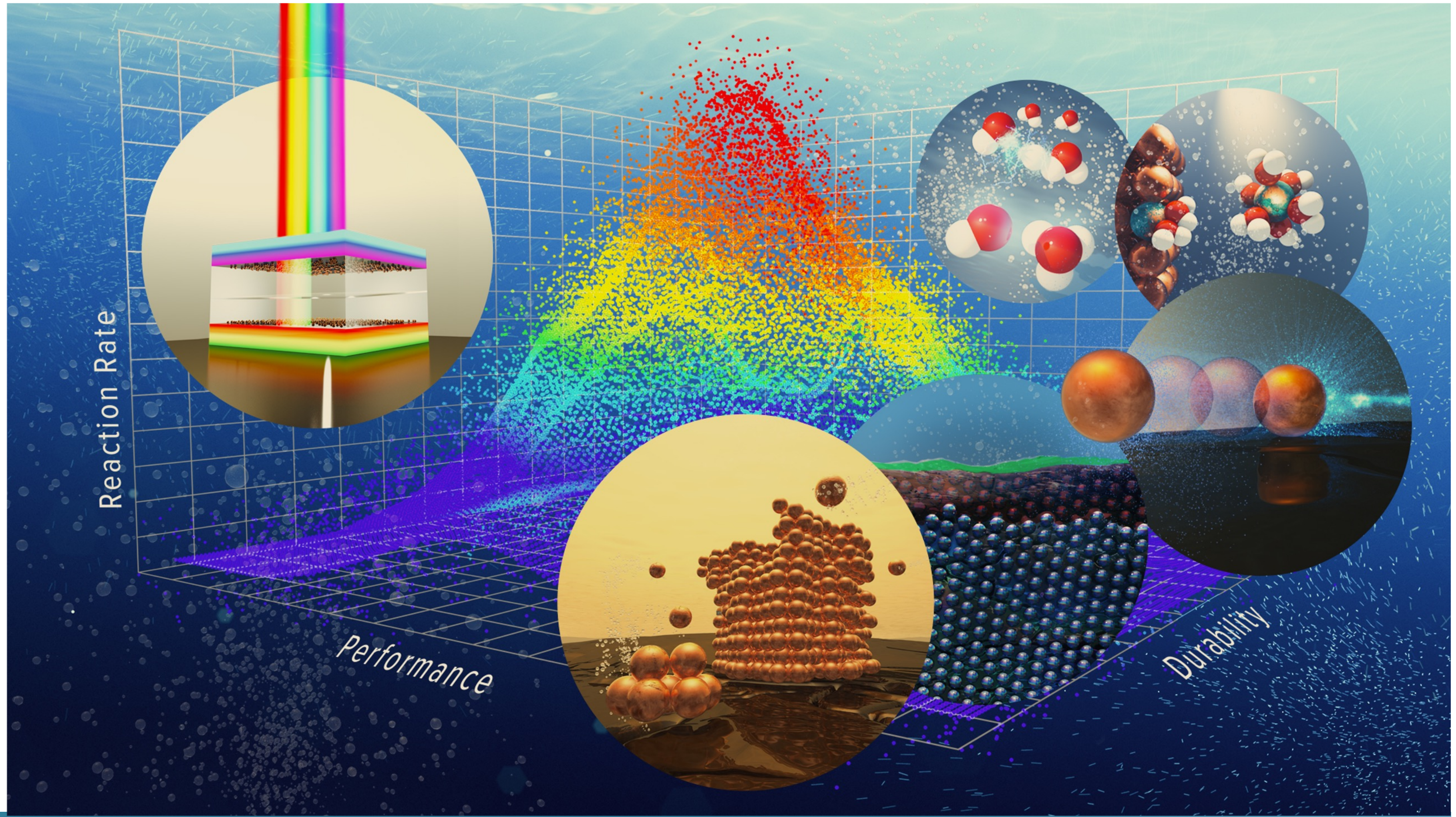
Photon, electron, and molecular processes from excitation to catalytic center





LiSA's Goals

Goal 3: Develop and validate predictive models for component and interface durability, and the implications for solar to fuel efficiency and selectivity under real-world conditions.



Goal 3: Develop models for component & interface durability and performance

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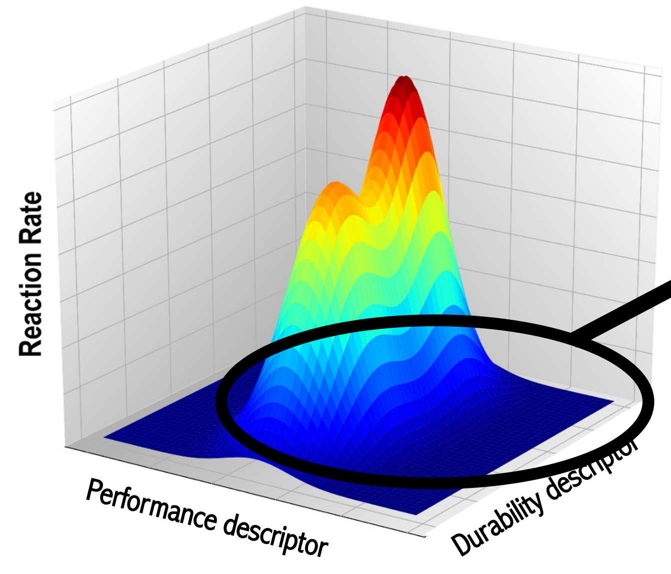
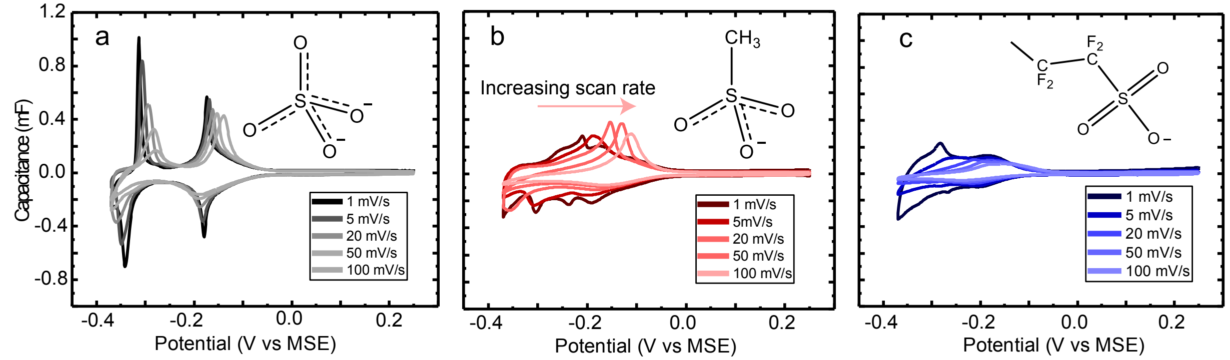
3
GOAL

Component and interface durability, and implications for STF, selectivity



Mechanisms of catalyst corrosion



- Cu^+ adions are stabilized by free sulfate and sulfonate
- Tethered sulfonate + polymer backbone disrupts the ordered adion layer

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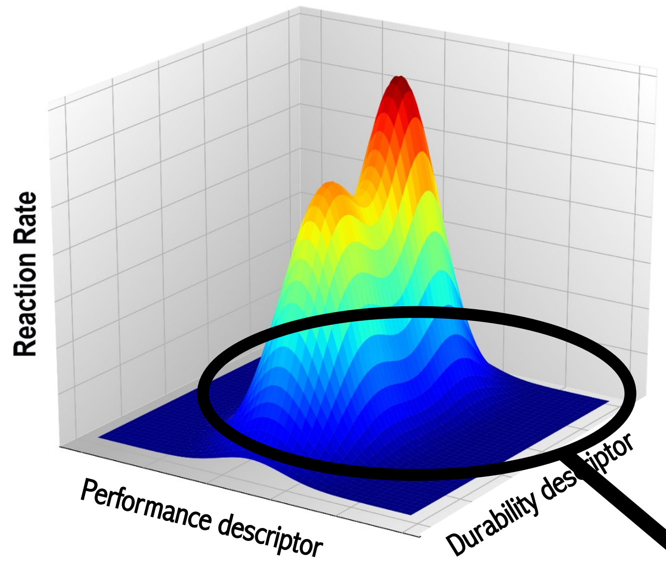
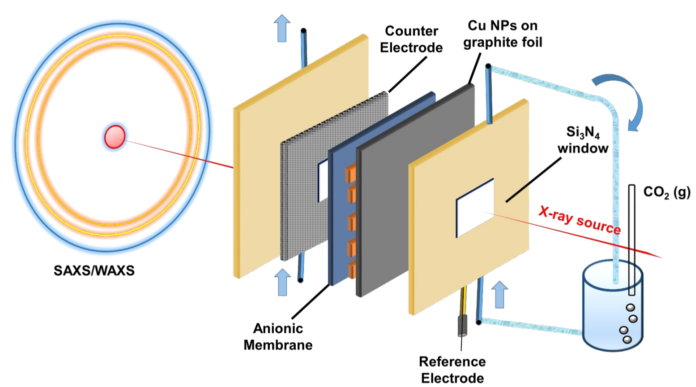
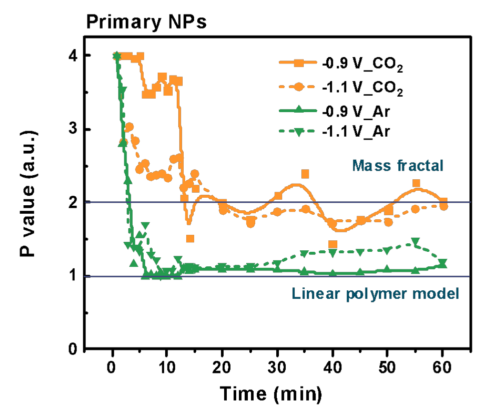
3 GOAL

Component and interface durability, and implications for STF, selectivity



Dynamics of Cu nanoparticle catalysts under operating conditions





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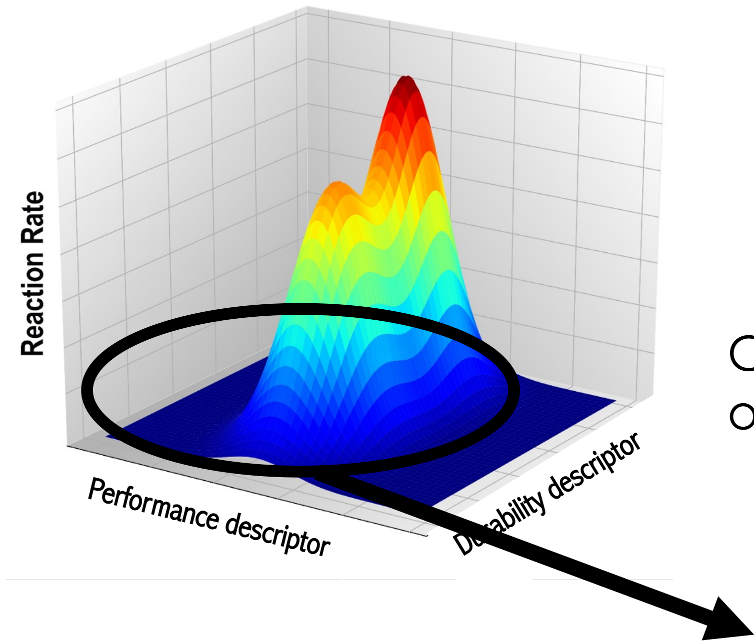
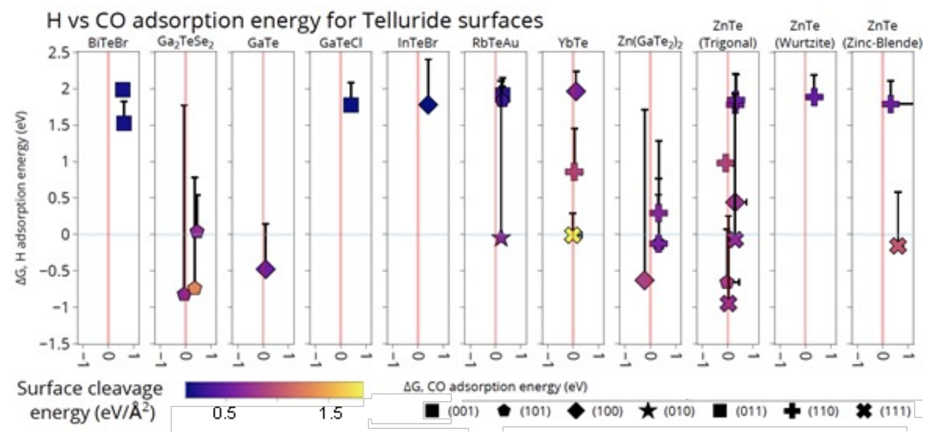
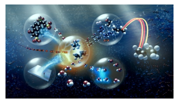


Chemisorption energies for 3 adsorbates (*CO, *H, *CHO) on over 300 sites of 39 surfaces of 11 Tellurium-containing materials

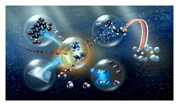


Project Plan

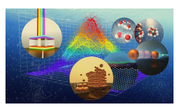
- Phase1: Microenvironment design
  - Control transport of water and ions



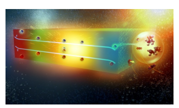
    - Water dissociation reactivity
    - Role of electrolytes
    - Local ions in catalytic microenvironments
  - Molecular design of microenvironments



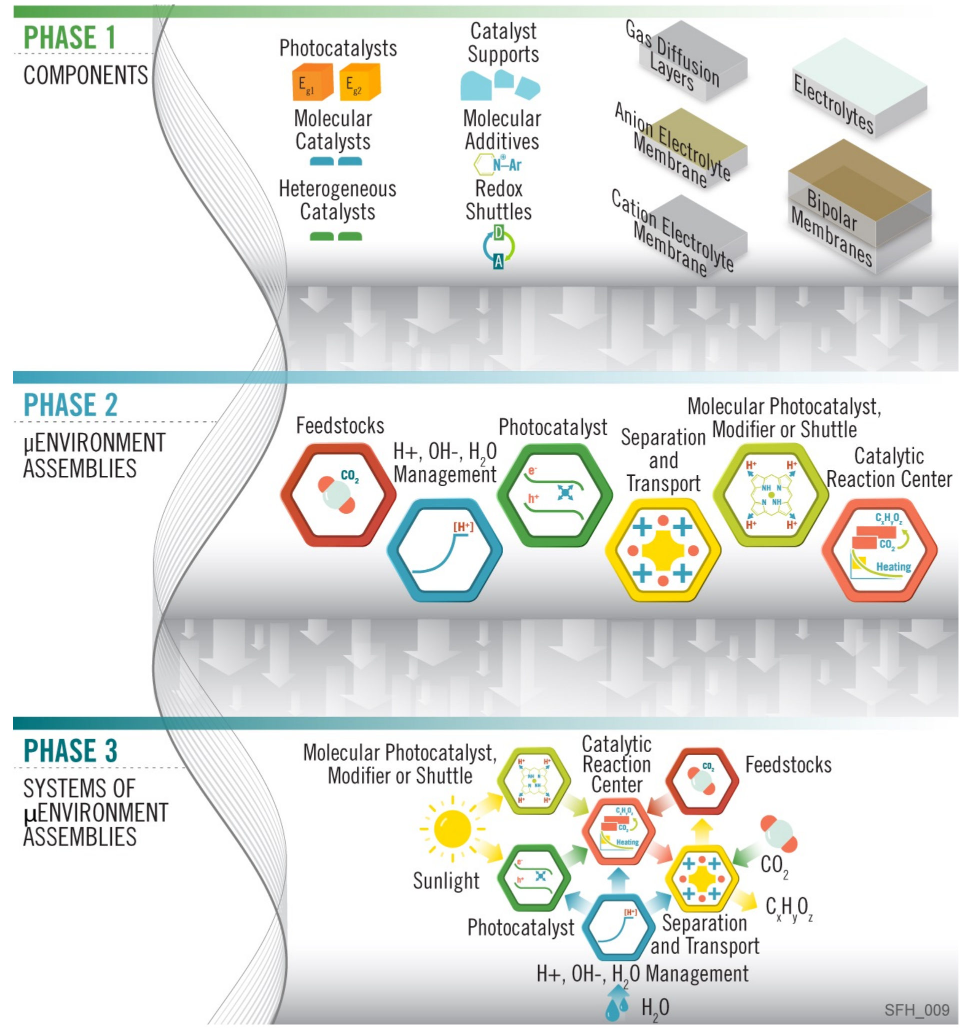
    - Catalyst selectivity when embedded in supports
    - Modified interfaces
  - Co-design of stable photoelectrodes



    - Defect and transport properties of nascent materials
    - Discover materials tuned for durability and activity
  - Understand charge carrier dynamics



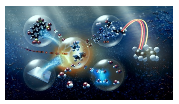
    - Probe and control dynamics across scales
    - Transport and potentials
    - Theory of excited state processes



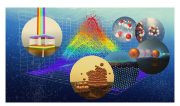
Laying the foundation for successful systems

Project Plan

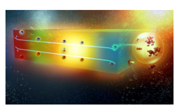
- Phase 2: Microenvironment exploration and integration
  - Co-design assemblies of microenvironments



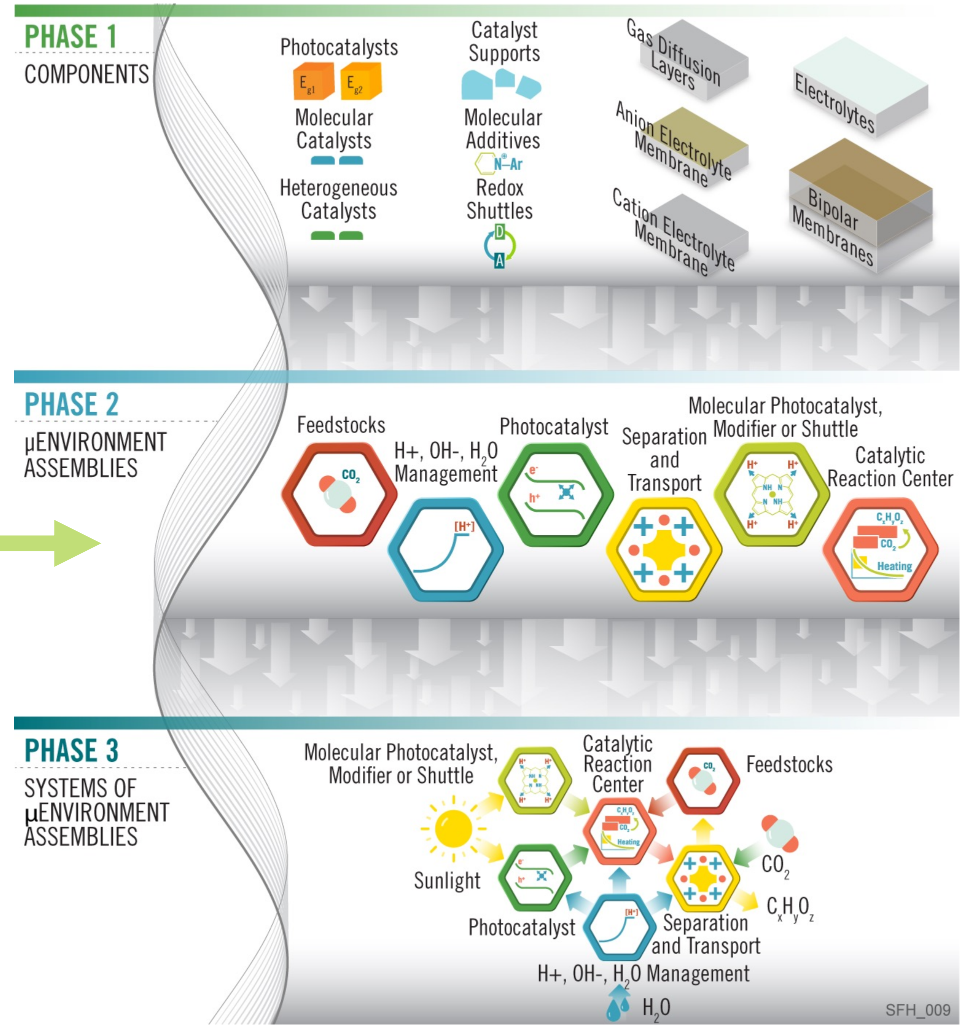
    - Operando techniques to probe components and assemblies
    - Architectures with enhanced selectivity by control in space and time
  - Light-driven processes to control reactions



    - Elucidate unique photocatalytic pathways
    - Principles of photon-mediated and photothermal processes
    - Using photoacids/bases to understand transport and mechanisms
  - Mechanisms of degradation



    - Identify interfacial processes underlying corrosion and deposition
    - Determine processes leading to sintering and migration



Evaluating how assemblies of microenvironments function

LiSA LIQUID SUNLIGHT ALLIANCE

Key LiSA Knowledge Advances 2023

1. Foundations of coupled microenvironment cascades
- 3TT & PEC/Thermocatalytic cascades

2. Interfacial modification to enable catalytic selectivity of Cu
- Molecular additives and ionomer coatings on cathodes

3. Ultrafast soft X-ray characterization of carrier dynamics
- Carrier relaxation dynamics in photoelectrodes

4. Surface instabilities of CO_2 reduction catalysts
- Relating catalyst morphology to corrosion mechanisms

5. Discovery of new photoelectrode materials
- $ZnTiN_2$ and amorphous Ni-Sb photoanode

DOE assignment to Fuels from Sunlight Hub, FY23

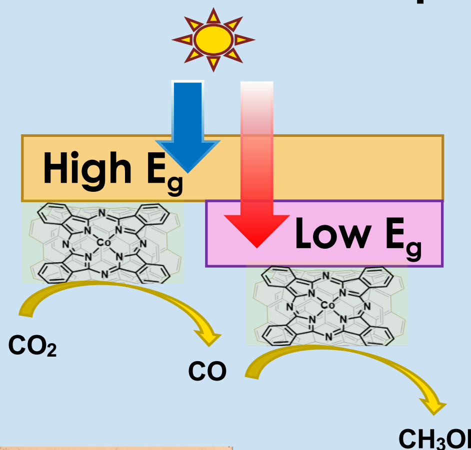
"Establish design principles, synthesize and integrate components, and evaluate the performance of 4 photochemical architectures that incorporate a light absorber and a multi-catalyst cascade to achieve CO_2 reduction to carbon-based fuels."

- Office of Management and Budget requirement
- CHASE and LiSA each deliver 2 architectures
- Quarterly report on progress
- Regular check-in meetings with CHASE and DOE

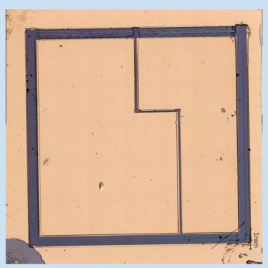
3-TERMINAL TANDEM TASK FORCE

Goal: Experimentally demonstrate a solar driven device with two coupled microenvironments to produce a liquid fuel

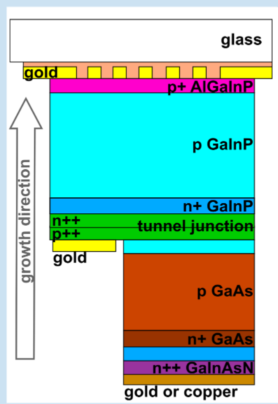
Three terminal tandem (3TT) cascade for liquid fuels



3TT solar cells provides the potentials needed for the cascade steps.
A single immobilized molecular catalyst (CoPc) drives both steps of the cascade.

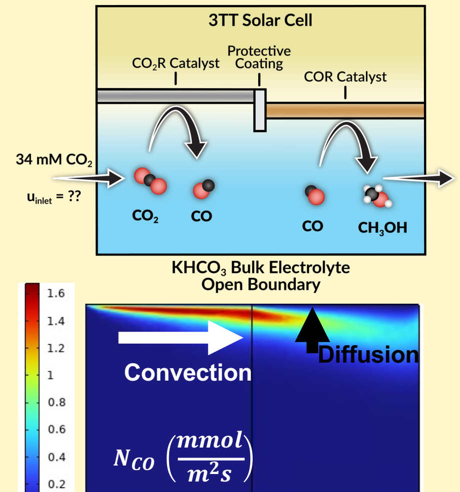


Inverted p on n structure enables catalyst integration with Au back contact

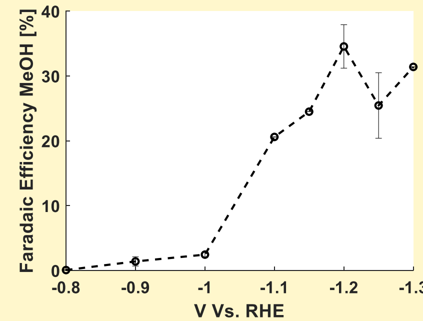


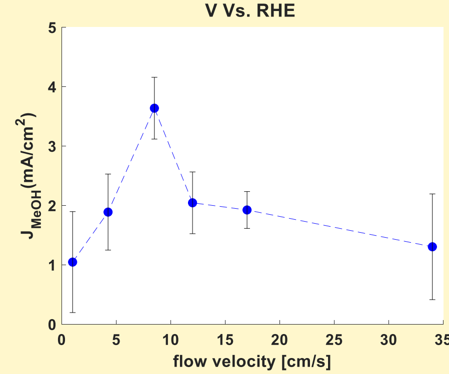
Importance of Microenvironments

For both single and tandem catalysts, potential and mass transport must be tuned for liquid fuel production

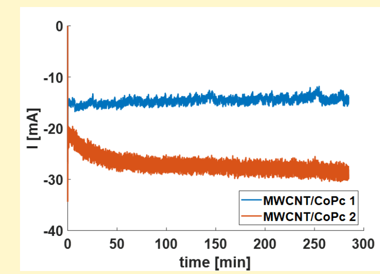


Continuum simulations show that efficient mass transfer of intermediates is critical.





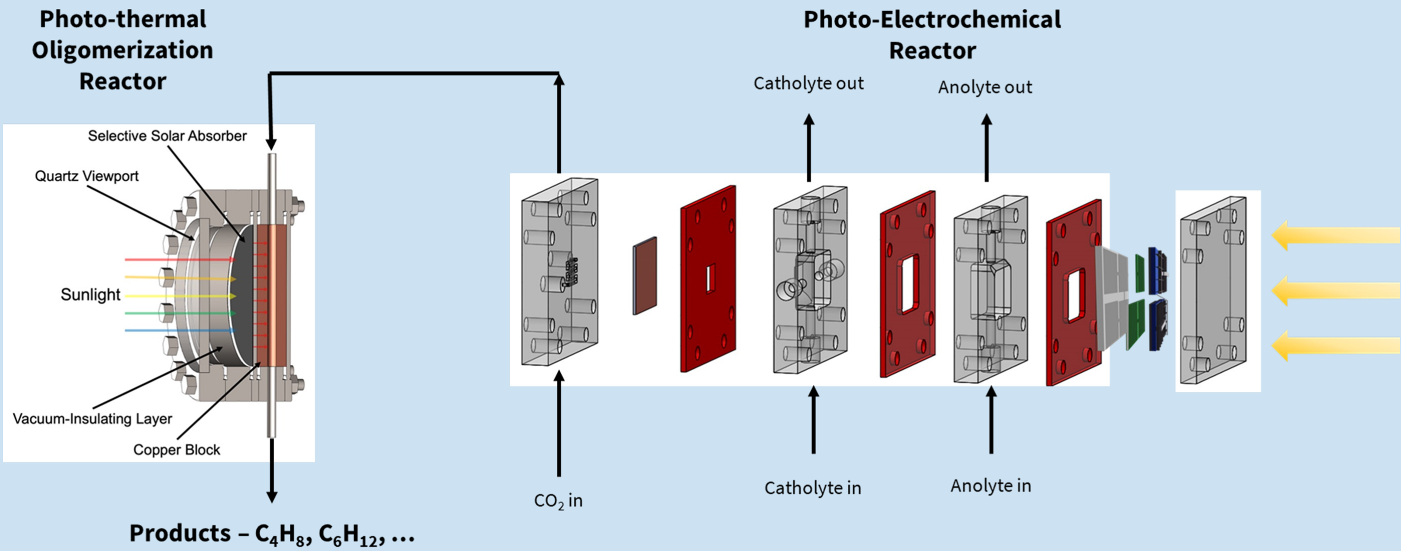
FE_{H2}= 83%
FE_{CO}=24%
>5% total FE to methanol



Substantial progress has been made towards realizing a solar-driven tandem cascade scheme to selectively make a liquid fuel, methanol, from CO_2.

Goal: To demonstrate the coupling of photoelectrochemical (PEC) and photothermal reactors to produce a liquid fuel from sunlight, CO_2, and water vapor

Tandem PEC/photothermal cascade for synthesis of liquid fuels



Operating conditions: PEC Reactor – 1 atm, 4 sccm CO_2, 2 ml/min 1 M KOH, 1 sun, 3 V, 60 mA/cm^2, Photothermal Reactor: 1 atm, 115 °C, 3-sun

Product composition

PEC Reactor: CO_2 conversion = 1%, Ethene Faradaic efficiency = 30%, Ethene concentration = 0.5%

Photothermal Reactor: Ethene conversion = 3%, butene selectivity = 98%, hexene selectivity = 2%

Next steps

Operate PEC/Photothermal cascade in a batch recycle mode to boost the conversion of CO_2 and the yield of hexene

Substantial progress has been made towards realizing a solar-driven PEC/Photothermal cascade scheme to selectively make a liquid fuel, hexene, from CO_2.

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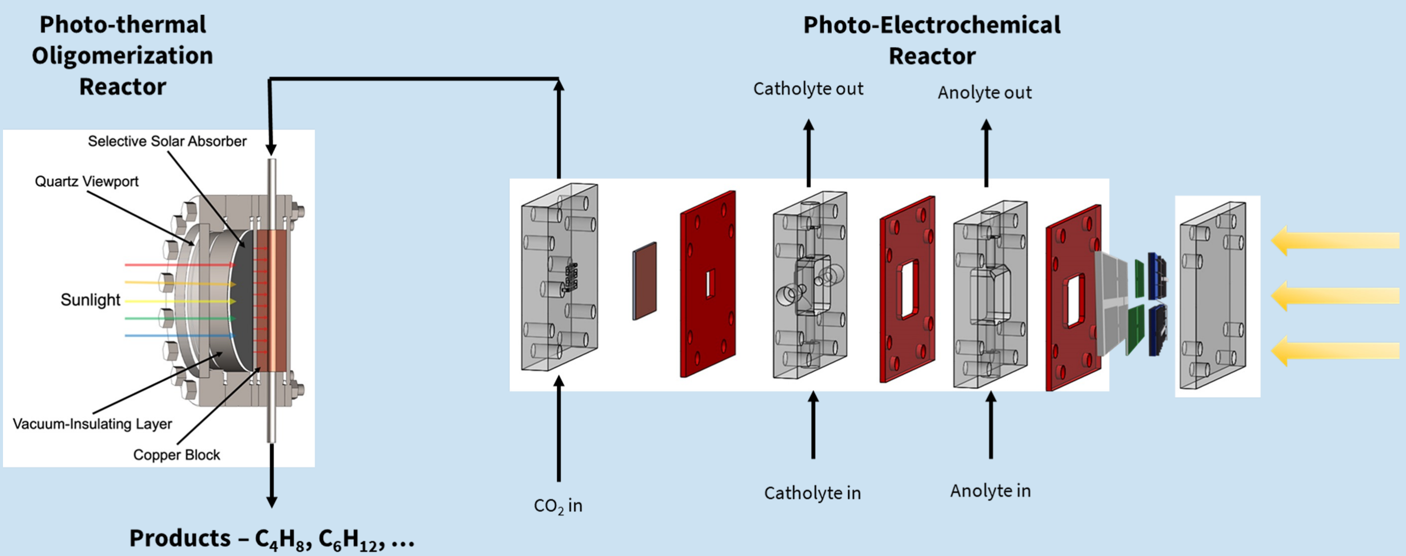

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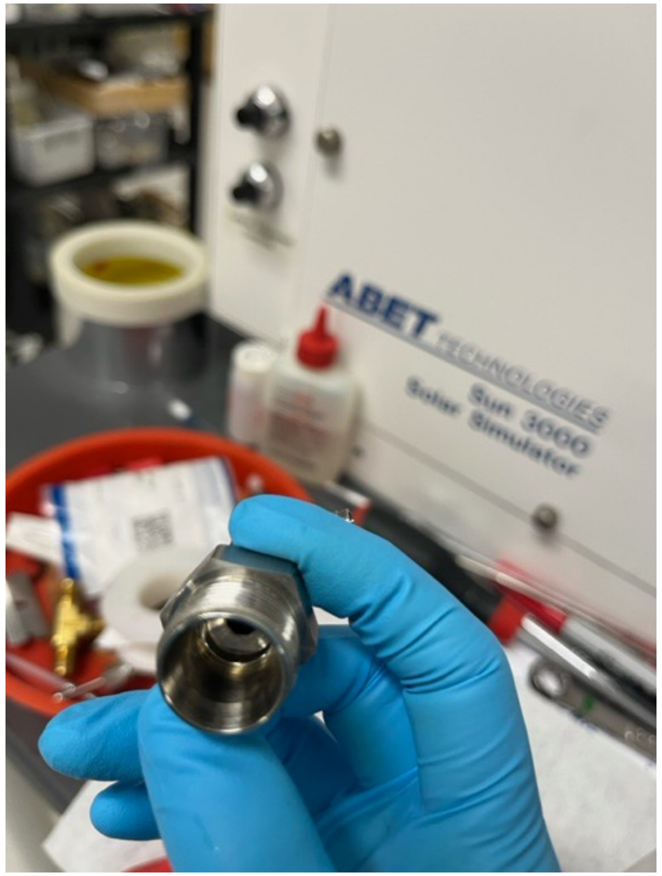

Substantial progress has been made towards realizing a solar-driven PEC/Photothermal cascade scheme to selectively make a liquid fuel, hexene, from CO_2.

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