Center for Light Energy Activated Redox Processes (LEAP)
EFRC Director: Michael R. Wasielewski
Lead Institution: Northwestern University
Class: 2009 – 2020

Mission Statement*: To develop the fundamental scientific understanding needed to use efficient light-driven multi-electron redox processes to power energy-demanding chemistry.*

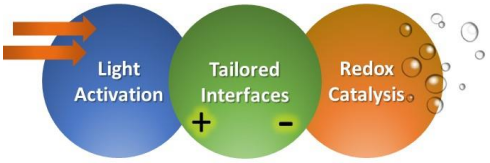

Fig 1. Synergistic LEAP Research Thrusts.

Understanding energy-demanding redox reactions is important because they are the basis of processes used on a global scale to provide materials, fuels, chemicals and food. Making these processes highly efficient will have a major positive impact on both the US and global economy. Leveraging the substantial advances made by the ANSER Center EFRC, LEAP Center research addressing our mission during the next two years is organized into three interwoven Thrusts with closely integrated approaches and team synergies:

- **Thrust 1. Powering Redox Processes.** Will produce charges at potentials required to drive energy-demanding redox reactions with temporal and spatial precision using unconventional organic/inorganic semiconductors.
- **Thrust 2. Tailored Interfaces and Hierarchical Assemblies.** Will tailor interfaces between **Thrust 1** semiconductors and **Thrust 3** redox catalysts using hierarchical assemblies to control charge flow to power the catalysts.
- **Thrust 3. Redox Catalysts for Energy-Demanding Reactions.** Will design, synthesize, and characterize molecules and materials with catalytic metal centers that will utilize charges provided by **Thrust 1** semiconductors to perform energy-intensive reactions, such as H_2O splitting, CO_2 and N_2 reduction, and C-C bond formation.

Thrust 1: Powering Redox Processes.

*The goal of LEAP **Thrust 1** is to leverage emerging classes of unconventional semiconductors to create charges at potentials sufficient to drive the catalysts described in **Thrust 3** to carry out energy-demanding redox processes. The interfacial strategies of LEAP **Thrust 2** will be used to couple the semiconductors to the catalysts and stabilize the overall system.* Achieving this goal will involve four types of closely related materials: organic semiconductors (Oss), perovskite semiconductors (PSs), quantum dots (QDs), and 2D dichalcogenides. These new semiconductors have recently astounded the energy conversion community with their long excited-state lifetimes, excellent charge mobilities, large photocurrents, broad optical absorption, chemical versatility, and the advancing stability. Specifically, OSs, especially as bulk-heterojunction structures, hybrid organic-inorganic halide PSs, QDs, and hybrid organic–2D inorganic materials have enabled major advances in fundamental understanding, many made by ANSER, which have resulted in greater extraction of photon energy with open-circuit voltages well above 1 V and fill factors near 80%. The approaches described here aim to achieve potential differences between extracted charges of up to 1.5-2.0 V to drive catalytic chemical reactions.

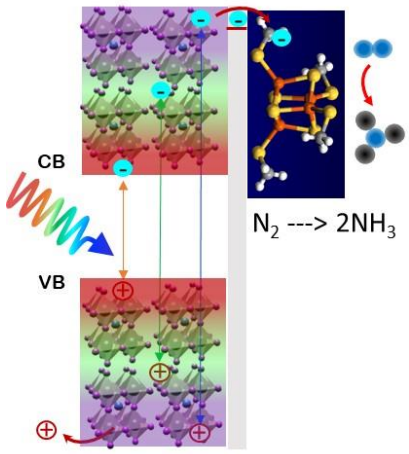

Fig 2. Schematic of interaction of a PS with an N_2 reduction catalyst, and hot-carrier extraction to catalytic sites via control of structure and recombination dynamics.

Thrust 2: Tailored Interfaces and Hierarchical Assemblies.

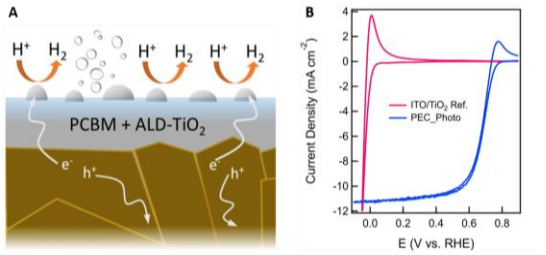

Fig. 3. A) Schematic of perovskite photocathode for proton reduction. **B)** I-V characteristics of ITO/PEDOT:PSS/halide-perovskite/PCBM/TiO_2/Pt in strong acid under simulated solar illumination vs an ITO/TiO_2/Pt control.

*The goal of LEAP **Thrust 2** is to understanding the interplay between materials and molecular chemistry to temporally and spatially control the flow of photo-generated charges to productive redox catalytic centers, while stabilizing all system components under conditions that are far from thermodynamic and chemical equilibrium.* To achieve catalysis of light-driven thermodynamically uphill reactions, **Thrust 2** aims to create and understand interfaces and hierarchical structures (Figure 3) that contain structurally and chemically well-defined linkers between light absorbers, redox catalysts, and electrodes, and that are robust under operating conditions. These structures will efficiently channel charge carriers into desired reaction pathways, minimize unproductive pathways and side-products, avoid high energy intermediates, and create states that store energy for triggered release.

Thrust 3: Redox Catalysts for Energy-Demanding Reactions.

*The goal of LEAP Thrust 3 is to design catalysts for efficient electron-driven chemical transformations—catalysts that can be interfaced/integrated (**Thrust 2**) with unconventional semiconductors (**Thrust 1**). Achieving this goal will involve understanding how light-powered molecular and heterogeneous catalysts, and their designed environments beyond the binding site, accomplish electron-driven, chemoselective transformations involving important molecular substrates such as CO_2 and N_2. These studies will yield efficient new catalysts, instructive new reaction mechanisms and pathways, and fundamental insights into the challenge of manipulating reaction networks in complex environments.*

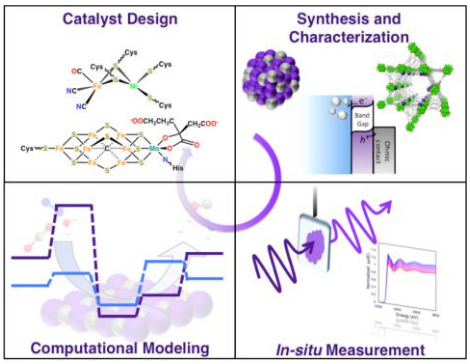

Fig. 4. Computational and experimental design, synthesis, characterization, and functional mechanistic assessment of atomically precise catalysts (**Thrust 3**) for integration (**Thrust 2**) with designed photoelectrodes (**Thrust 1**).

Thrust 3's approach (Figure 4) will integrate theory and experiment to: a) design catalysts; b) develop new ways to synthesize desired catalysts; c) characterize designed catalysts *in operando*; d) evaluate complex mechanisms; and e) measure catalyst chemoselectivity and energy efficiency against theory. The precept is that mechanistic understanding of specific reactions will yield transferable design rules for existing and potentially new classes of catalysts and reactions.

Center for Light Energy Activated Redox Processes (LEAP)	
Northwestern University	Michael Wasielewski (Director), Omar Farha, Mark Hersam, Joseph Hupp, Mercouri Kanatzidis, Tobin Marks, George Schatz, Emily Weiss
Argonne National Laboratory	Michael Pellin (Deputy Director), Lin Chen, Alex Martinson
Yale University	Victor Batista, Gary Brudvig, Robert Crabtree, James Mayer, Sharon Hammes-Schiffer

Contact: Michael R. Wasielewski, Director, m-wasielewski@northwestern.edu
847-467-1423, http://www.LEAP-Center.org