Report of LBNL Solar Workshop March 28/29, 2005

1. Opening Plenary Session

The opening plenary session of the workshop featured an overview by Laboratory Director Steven Chu on the urgency for moving toward a sustainable, CO_2 neutral energy economy, and a call for tackling the most challenging scientific questions of making cheap solar fuel and electricity a reality. The presentation was followed by an outline of possible strategies for working toward a CO_2 neutral energy economy by Daniel Kammen (UC Berkeley Goldman School of Public Policy), and on policy issues of a transition toward a renewable fuel economy by Mark Levine, Director of LBNL's Energy and Environmental Technologies Division. Two external experts educated the workshop participants on crucial aspects of solar to fuel: Art Nozik (National Renewable Energy Laboratory) on the maximum attainable efficiencies of various solar to fuel scenarios, and Tom Moore (Arizona State University) on the prospects of bio-inspired approaches to large-scale solar generation of fuels.

2. Breakout Session

Synthetic Biology; Engineered Organisms for Biomass to Fuel and Solar to Chemical

Biomass, mankind's long-standing energy source has the potential of supplying significant amounts of renewable energy if efficiencies for the conversion to fuels can be substantially improved. The talks and discussion of the session identified three major challenges that need to be addressed successfully in order to make solar to fuel using organisms a viable option. (1) Currently practiced corn-to-fuel is not sustainable because the overall process consumes more energy in the form of fossil fuel than available from the corn ethanol itself. Furthermore, the corn to ethanol agricultural process is accomplished by substantial water pollution and atmospheric emissions that render it environmentally unsustainable. (2) Cellulose, the largest available biomass resource remains untapped. (3) Direct solar hydrogen from cyanobacteria and green algae is currently limited by the low light to fuel efficiency of these natural systems.

The following research needs were identified to address these challenges. (1) Engineering of new organisms is needed for on-site production of fertilizers, especially photosynthetic nitrogen fixation in the form of ammonia. This will improve the energy balance for corn to fuel by avoiding the large fossil fuel consumption by conventional manufacturing processes and fertilizer transportation. Also, more sustainable sources of phosphorous have to be found. (2) Novel metabolic pathways need to be engineered for the conversion of cellulose to fuel (ethanol, methanol, methane, hydrogen). Possible approaches include the design of an organism with an artificial chromosome that incorporates the relevant features of the cellulose degrading machinery. A vast untapped source for establishing such pathways are the natural organisms whose metabolic capabilities are not yet known (approx. 90% remain unexplored). Solar light-driven engineered proton pumps to generate chemical energy by the buildup of proton gradients for the production of ATP is a key concept for accomplishing cellulose to fuel conversion, or for the fixing of CO_2 in the form of ethanol using cellulose and other biomass as electron source. Thermodynamic evaluation of each step will be crucial for obtaining an efficient system. (3) Engineering of green algae and cyanobacteria with improved photosynthesis rates, and on-site coupling of hydrogen production to catalytic conversion to C-based fuels are important targets. (4) Bio-inspired synthetic catalysts for key bond forming and breaking steps for fuel formation and interconversion of various forms of fuels. Enhancement of the stability and increase of the rates compared to natural catalysts through synthetic modification and use of nanostructured catalyst supports is an important goal. Development of efficient methods for coupling of catalysts to electron or hole source, and embedding in robust nanostructured supports for enhanced stability are crucial tasks.

Engineered Systems; Hybrid Nanomaterials, Biomimetic Systems for Solar to Fuel

Artificial photosynthetic devices for solar to fuel offer the potential of robust and efficient systems not limited by the constraints of living organisms. The formal presentations and discussion of the session identified two main areas where major challenges need to be met in order to achieve this goal. One area is biomimetic catalysts that accomplish similar multi-electron transformations as natural systems, such as H_2O oxidation to O_2 or CO_2 reduction to a C-based liquid fuel, but function at much higher rates and are more robust. There are currently very few engineered catalysts that accomplish these fuel forming transformations. Most require noble metals whose insufficient abundance precludes their use in a large scale energy economy, and almost all are driven by stoichiometric reagents rather than by visible light. Progress is hindered by a lack of understanding of the bond making/breaking steps and coupled proton and electron transfer events at catalytic sites. A second major challenge is bio-inspired supramolecular assemblies that afford optimum coupling of light-harvesting, charge migration and catalytic components for efficient fuel formation.

The participants considered the following main research needs: (1) Development of synthetic catalysts with abundant low Z metals (Mn, Fe, Co, Ni, Cu, Zn) for the splitting of water, reduction of CO_2 to formic acid and ultimately to methanol, or for the formation of halogens from hydrogen halides. Key aspects are multi-electron transfer capability and control of proton and electron transfer, design of which will benefit greatly from insights gained by structural and mechanistic studies of biological catalysts. (2) Exploration of methods for increasing the durability of biomimetic catalysts, such as encapsulation or anchoring on inorganic supports and establishing mechanisms for self repair. (3) There is a need for exploring organic or biological/organic 3-D hybrid structures for integration and optimal organization of the photoactive and catalytic moieties, taking architectural design principles of nature as a guide. (4) Another important solar energy storage mode that can be exploited in such bio-inspired supramolecular assemblies is light-driven generation of ion gradients across membranes, requiring the development of synthetic proton pumps.

Nanomaterials and Nanostructured Assemblies for Photochemical Conversion (Solar to Electric and Solar to Fuel)

The emergence of nanotechnology and the rapid advances in the development of novel nanoscale and nanostructured materials has opened up unprecedented opportunities to overcome long-standing obstacles toward efficient conversion of solar light to electricity and fuels. Major obstacles include: (1) Efficient absorption of photons from the full solar spectrum. (2) Durability of light harvesting and fuel forming sites, and of supports for the vectorial arrangement of the various components. (3) Efficient contacts between photo-active charge-transfer components and catalytic sites. (4) Spatial separation of the chemical products generated at oxidizing and reducing sites to prevent efficiency-degrading back or cross reactions. (5) Materials suitable for inexpensive fabrication and processing of solar to electric or solar to fuel assemblies on a very large scale.

A concerted effort should be launched to bring to bear advances in nanoscience and technology on these challenges. In particular, novel approaches by nanostructured materials should be explored to control the fundamental processes such as absorption of light and the density of photon, electron and phonon states to maximize the use of solar radiation. New types of nanomaterials need to be engineered that minimize the loss of charge, particularly in the promising area of metal oxide and metal sulfide semiconductor systems. 3-D inorganic or organic/inorganic hybrid nanostructures should be explored to control the transport of chemicals in photosynthetic systems to avoid loss by cross reactions, and to achieve integration of the functional components with precise arrangement for optimal coupling. Such materials might offer strategies that will enhance robustness through recycling of degraded organic components during operation. Nanoscale engineering needs to be developed for improved charge contacts at interfaces and between surfaces and molecular components, including biological functionalities on inorganic supports. This is an important prerequisite for the integration of multi-electron transfer catalysts into nanoscale materials. Effort should focus on exploiting nanotechnology for designing solar to electric or fuel device fabrication that resembles plastic manufacturing.

Photoelectrochemistry

The participants of this breakout session identified the lack of efficient multi-electron transfer catalysts for water oxidation and proton or CO_2 reduction as the single most critical challenge of efficient photoelectrochemical fuels generation (methanol, methane, hydrogen). Whether considering photovoltaic coupled to electrochemical devices or photoactive electrodes of photoelectrochemical cells, the performance of all existing systems is limited by the inefficiency of the fuel forming transformations at the electrodes.

There is a need for the design of engineered enzymes that catalyze the above redox reactions at the appropriate potential and at substantially higher turnover rates compared to natural catalysts. Another important engineering aspect is improved stability over the biological systems. The effort requires a close collaboration between chemical biologists and inorganic and materials chemists.

3. Themes for Berkeley Lab Solar to Fuel Initiative that Emerged from the Plenary Discussion Session

Three preliminary research themes that build on unique Berkeley strengths emerged from a half-day plenary discussion that followed the breakout session.

Fuel-Forming Catalysts

A cross-disciplinary effort among chemists, biologists, spectroscopists and computational scientists focuses on novel catalysts that accomplish the demanding transformations of water and carbon dioxide to fuels, and efficiently convert one fuel to another. Tasks involve

- Development of synthetic low Z metal catalysts for efficient multi-electron oxidation/ reduction of H_2O and CO_2 to H_2, O_2, and C-based liquid fuels on electrodes, upon integration into supramolecular assemblies for direct solar to fuel, or incorporation into engineered organisms for biomass to fuel conversion. Catalysts for CC, CO, OH bond making or breaking for facile interconversion of various forms of fuel, including the conversion of carbohydrates to fuels. Catalyst for N_2 activation for on-site nitrogen fixation in biofuel production. Guidance from the understanding of biological catalysts coupled with mechanistic and computational effort will be crucial.
- Modification of biological catalysts by synthetic components for improved turnover rates, durability, and facile integration into nanostructures for coupling to charge-transfer and light harvesting components. Development of methods for efficient contact between catalytic site and electron/hole source.

Breakthroughs in catalytic efficiency is the single most consequential factor for achieving economically viable scenarios for solar to fuel.

Engineered Organisms for Fuels from Biomass and Sunlight

Synthetic biologists, materials chemists and catalysis groups explore engineered organisms for the generation of fuels from biomass and sunlight. Tasks involve

- Development of engineered organisms for the conversion of cellulose and waste to fuel.
- Engineering of solar light-driven proton pumps for use as energy source in synthetic organisms for biomass to fuel conversion. Targets include the fixation of CO_2 to ethanol in yeast using biomass as electron source.
- Synthetic modification of green algae and cyanobacteria for increased photosynthesis rates, and coupling of the hydrogen production to catalytic conversion to a C-based fuel.

The economic viability of biomass as energy source would gain substantially if the large untapped feedstock of cellulose and waste were put to use, and if on-site photosynthetic generation of fertilizers would make biofuel production a net solar to fuel conversion process.

Integrated Assemblies for Solar to Fuel or Electricity through Nanoscience and Nanotechnology

Synthetic inorganic, organic and catalysis groups join solid state physics, materials and nanotechnology groups to integrate photoactive and catalytic components into robust artificial assemblies for efficient electricity or fuel production. Tasks include

- Development of inorganic or hybrid solar cells with enhanced efficiency for light absorption, charge separation and charge collection based on breakthroughs in optical engineering on the nanoscale.
- Design of metal oxide and metal chalcogenide nanostructures for direct solar to fuel.
- Exploration of 3-D organic, inorganic or hybrid nanostructures for integration and optimal coupling of light harvesting, charge separating and catalytic components for direct solar fuels production. Development of methods for self assembly and for preparing such structures in the form of membranes (artificial leaf).
- Development of built-in recycling capability for organic components in order to enhanced durability.

The economic feasibility of solar fuels depends on the development of integrated assemblies that can be manufactured cheaply on a very large scale.