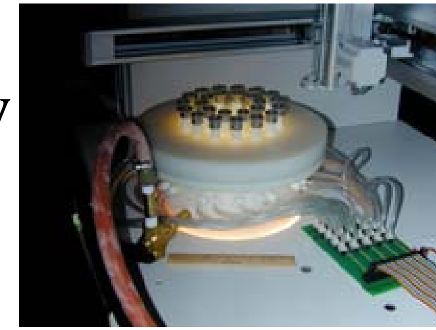
Discovery of Photocatalysts for Hydrogen Production

2004 DOE Hydrogen Review
May 24-27th, 2004
Philadelphia, PA



Theodore Mill, Albert Hirschon, Michael Coggiola and Brent MacQueen (PI)
SRI International, Menlo Park, CA
Nobi Kambe, NanoGram Corporation, Freemont, CA
Timothy Jenks, Neophotonics, San Jose, CA

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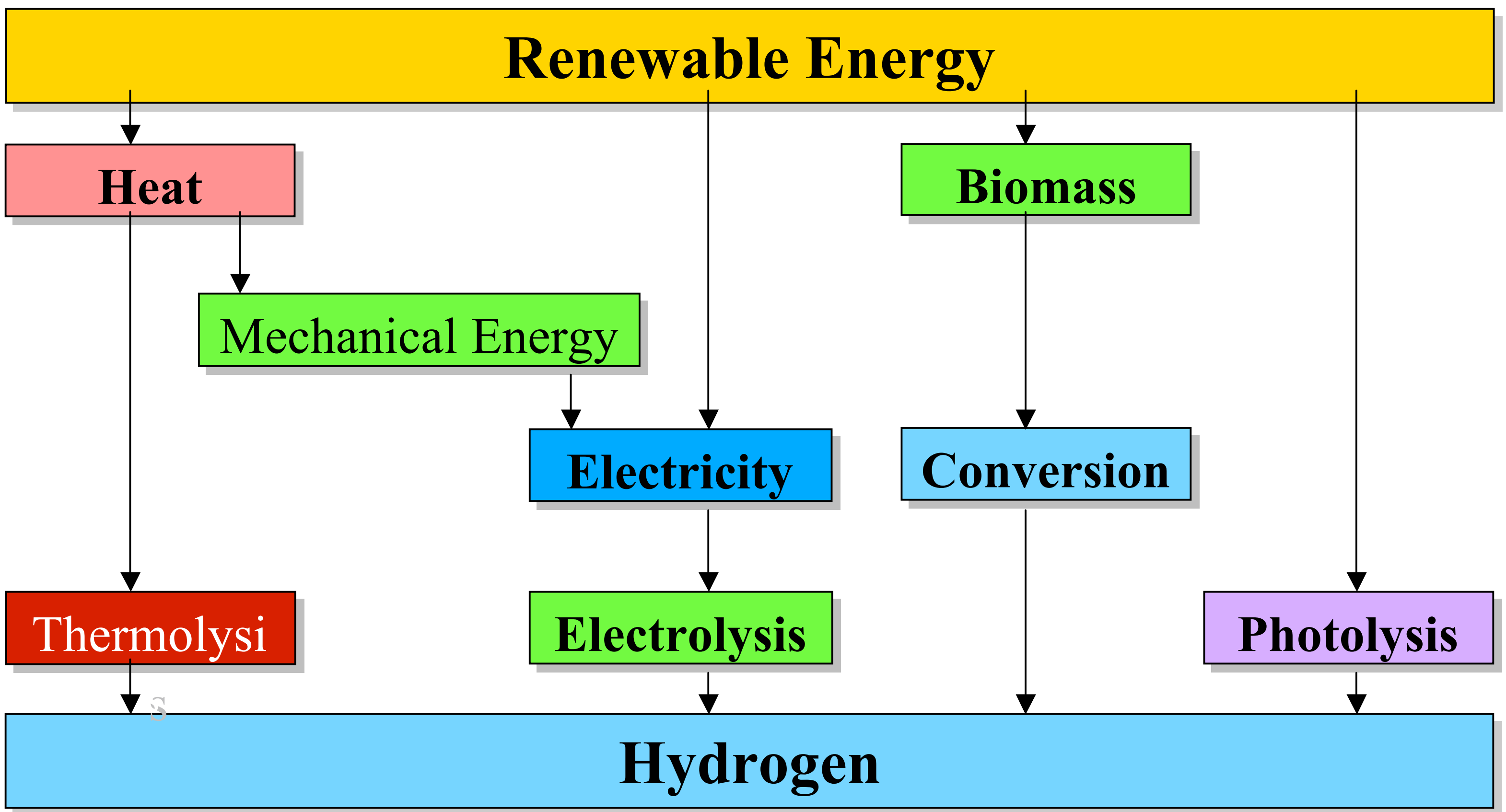
Sustainable Paths to Hydrogen



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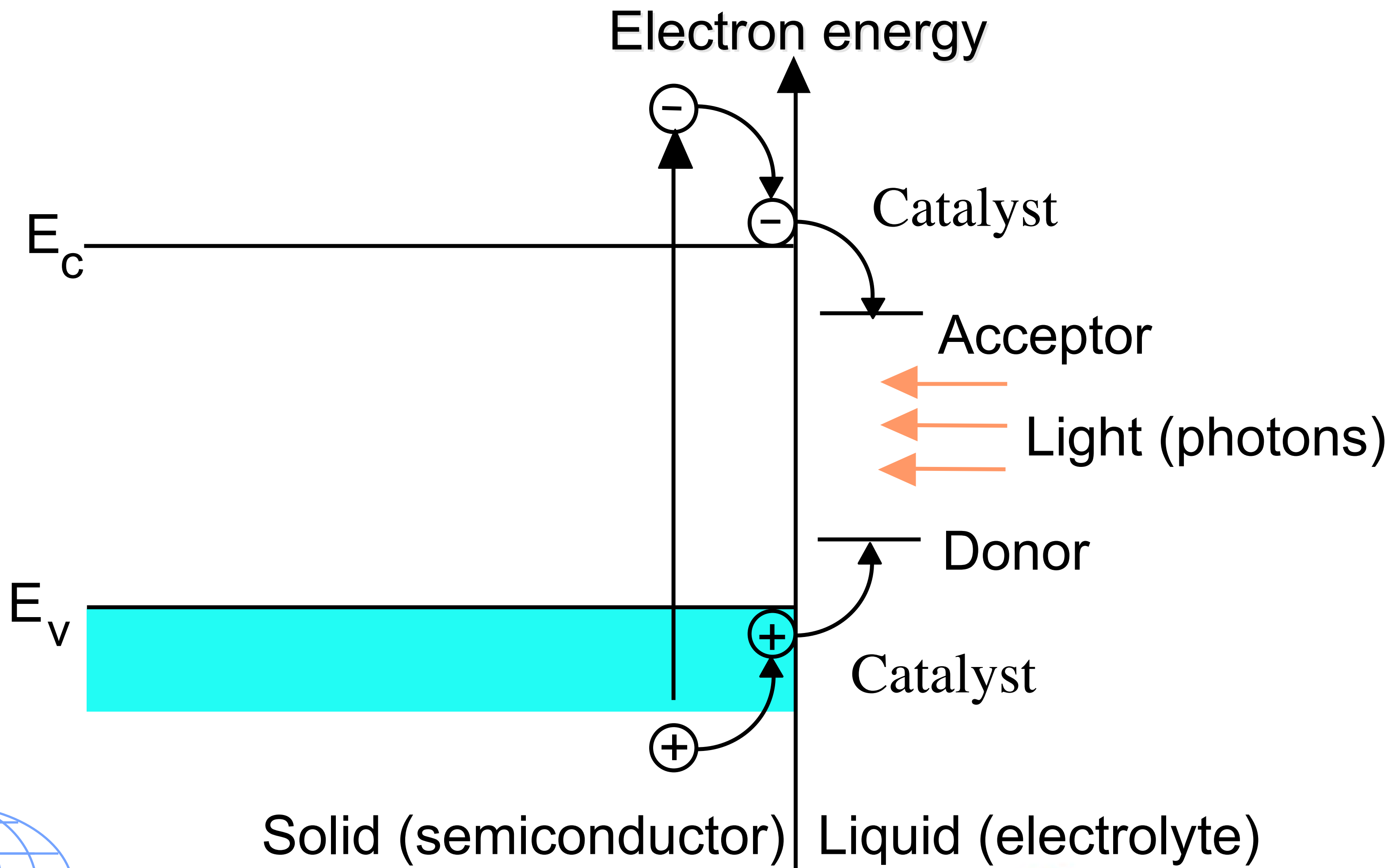
PEC 101



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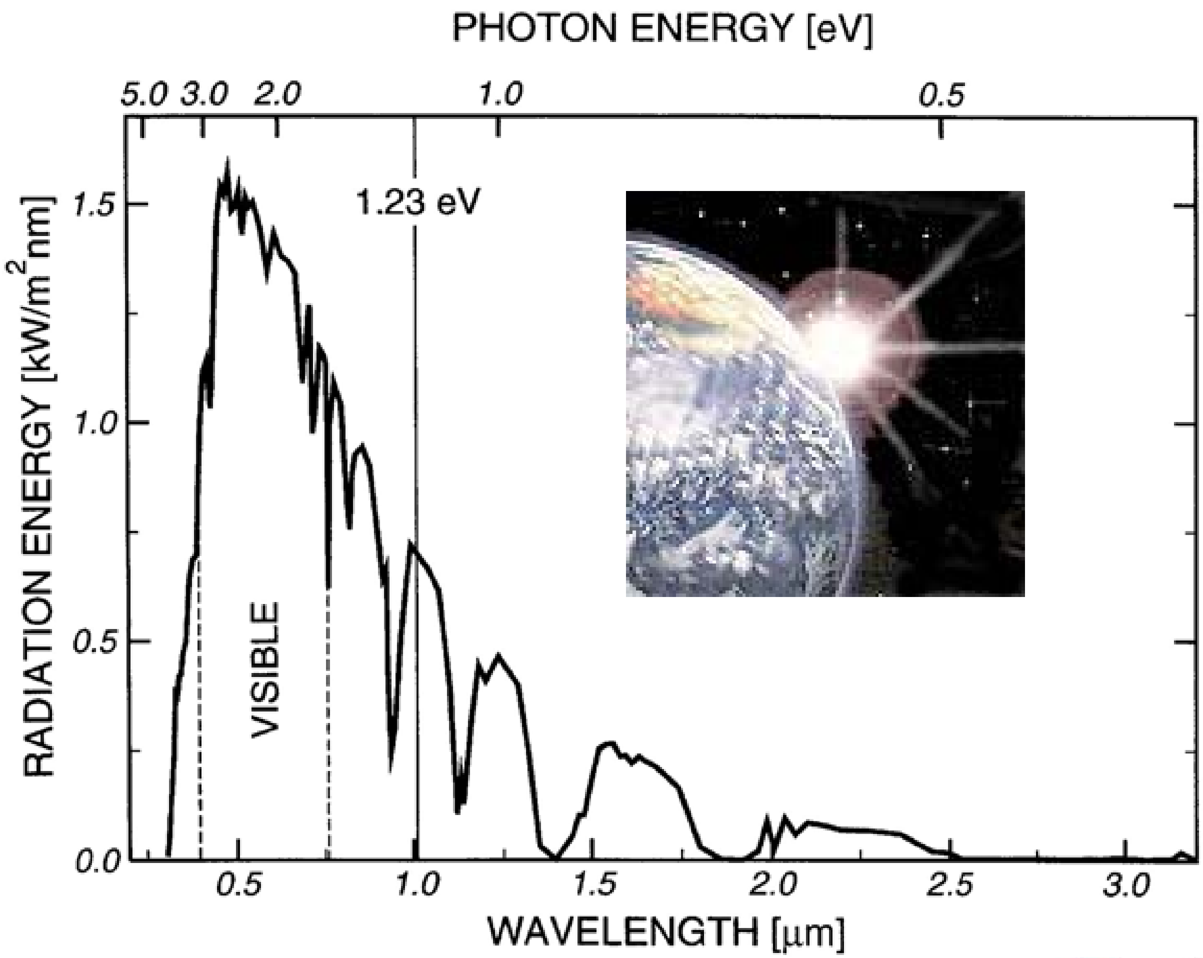
Bandgap Considerations



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Relevance/Objective: Technical Barriers

Key Technical Barriers are Materials and Systems Engineering Related

- **Efficiency (band gap and edges), Durability and Cost**

Materials need to be found that address these issues.

This project will assist in the identification of materials that directly address these barriers.

Specifically, the discovery of low cost materials with improved efficiency will be a driver to lower cost PEC hydrogen.

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Relevance/Objective: Technical Targets

Characteristics	2003 Status	2005 Target	2010 Target	2015 Target
Solar-to-hydrogen Efficiency	7%	7.5%	9%	14%
Durability	100 h	1,000 h	10,000	20,000
Cost	N/a	360	22	5

Targets for 2005 and 2010 involve sequential order of magnitude improvements in durability and modest improvements in efficiency.

Meeting these targets will require improvement of efficiency of existing highly durable oxide components, systems engineering to reduce cost of efficient multi-junction designs or a combination thereof.

The materials discovery required to meet the Technical Targets will be expedited by the use of high throughput screening tools being developed in this project. Furthermore, the inclusion of a partner with the means to produce commercially relevant amounts of materials will hasten the development required to make PEC hydrogen viable.

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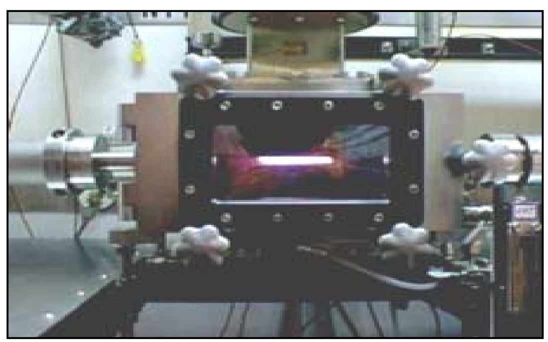
Approach

- Develop tools that will allow for the high throughput analysis of materials prepared with commercially relevant synthetic means with respect to PEC hydrogen.
- Use Neophotonics/NanoGram's laser pyrolysis to prepare new materials (composition/phase/particle size) for screening with respect to PEC hydrogen.



Close-up: NanoParticle Laser Reaction Chamber

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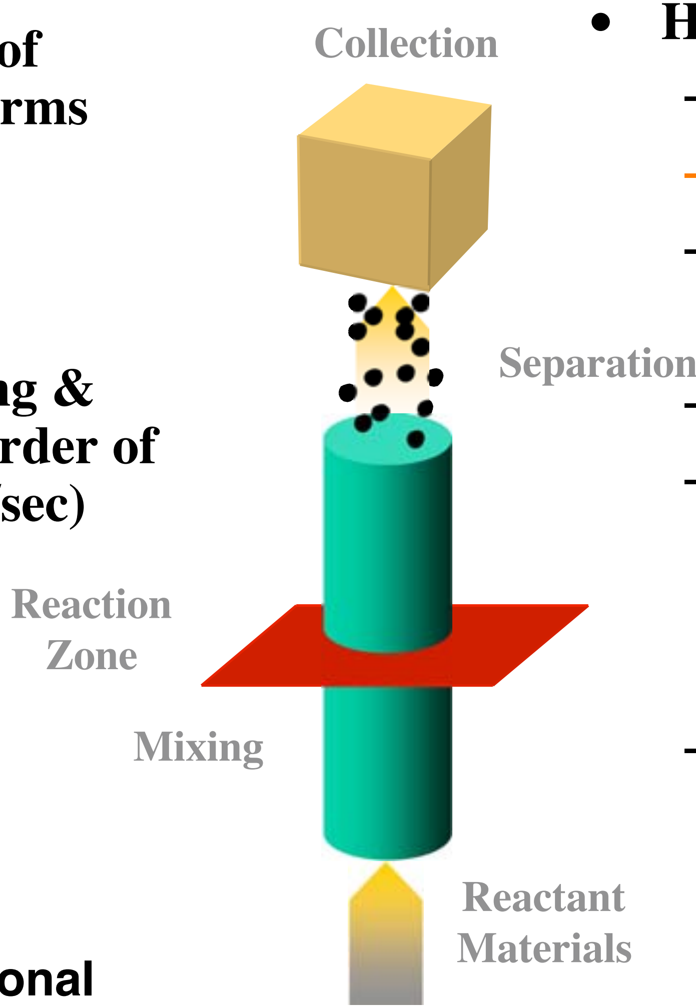
Laser-driven Nanoparticles Synthesis

- **Wide range of precursor forms**
  - **Gas**
  - **Vapor**
  - **Aerosol**
- **Rapid heating & quench (at order of 10^5 degrees/sec)**



- **Huge materials portfolio**
  - **Crystalline inorganics**
  - **Multi-element compounds**
  - **Tightly controlled size**
  - **High chemical purity**
  - **Oxide, sulfide, nitride, metal, phosphate, carbide, silicate inorganic compounds...**
  - **Rare earth-doping at high concentration**
    - **Scalable over 1kg/hr per equipment**

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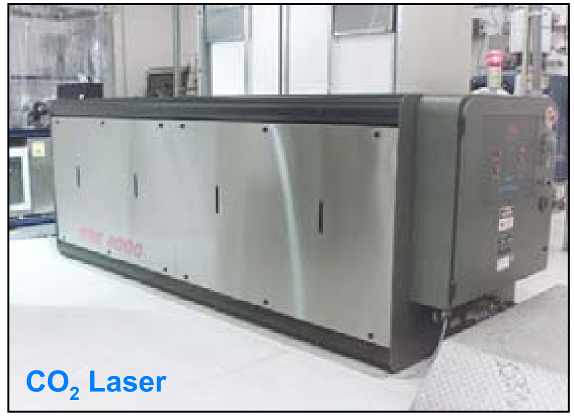
Scalability

High Volume Production System

LRD Reactor



CO_2 Laser

Controller

Scrubber System

Chemical Delivery System

- **Industrial; mass production**
  - **up to 10,000 wafers/year/system**
- **Fifth-generation technology**

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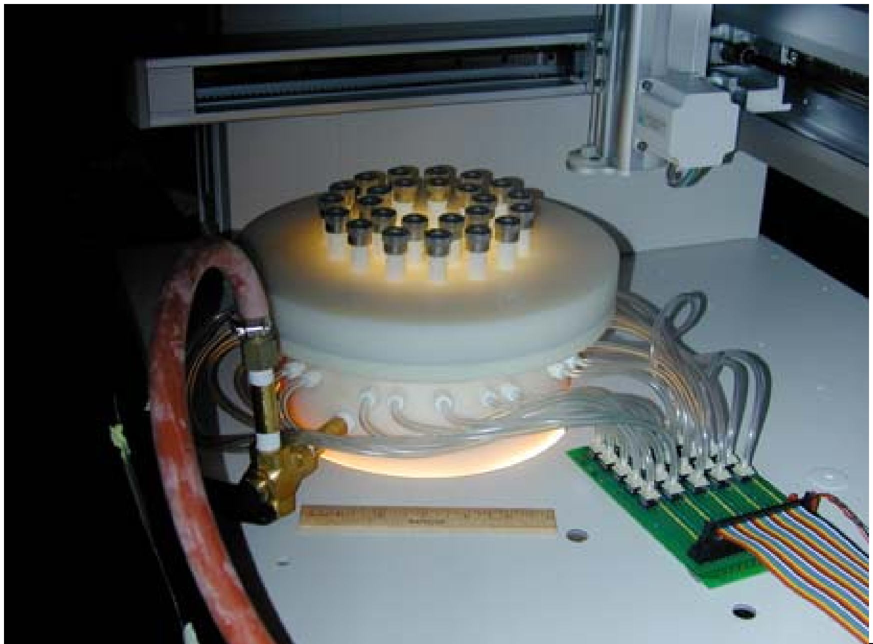
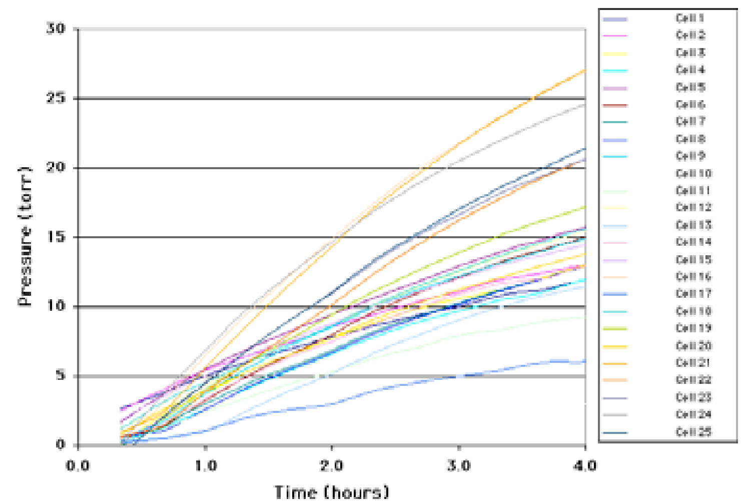
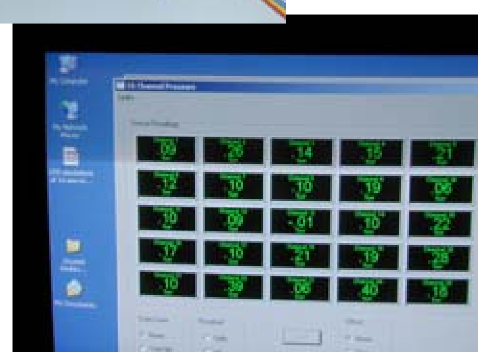
Approach (concl.)







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Safety

- Nanoparticle synthesis
  - Computer controlled system has a range of interlocks for safe operation including start-up, in-process upsets, and during shutdown
  - All nanoparticle production, collection, equipment cleaning is carried out inside a fume hood
  - Respirators are used when handling nanoparticles and nanoparticle-exposed equipment
  - Safety interlocks, beam guiding shields, and engineering controls are in use for laser safety; Beam alignment and adjustments are only done by certified Laser Safety Officer
  - Reactants, and precursors are contained in exhausted gas cabinet with sensors to detect leakage
- Photolysis Experiments
  - Light source is fully shielded
  - Sacrificial electron donor used, no Oxygen generated
  - Hydrogen Sensor (Neodyn) on pressure transducer board shuts down system if H_2 concentration above 0.2% detected.

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Project Timeline

Project initiated in October 2001 as three year effort to develop tools and investigate new materials.

Business decisions of partner on project resulted in year 1 being 17 months and equipment delays resulted in Year 2 being 16 months. Spending to date and funding requested are summarized below:

Source Year	1	2	3 (est.)
DOE	250K	320K	360K
Neophotonics/NanoGram	62K	80K	90K
Total	312K	400K	450K

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Timeline (cont..)

8/01 to 1/03	2/03 to 6/04	7/04 to 6/05
Phase One	Phase Two	Phase Three
1 2 3	4 5 6 7	

Phase One

1. Solar Simulator Constructed
2. 4 cell photolysis analysis module constructed
3. Photolysis analysis module expanded to 24 cells

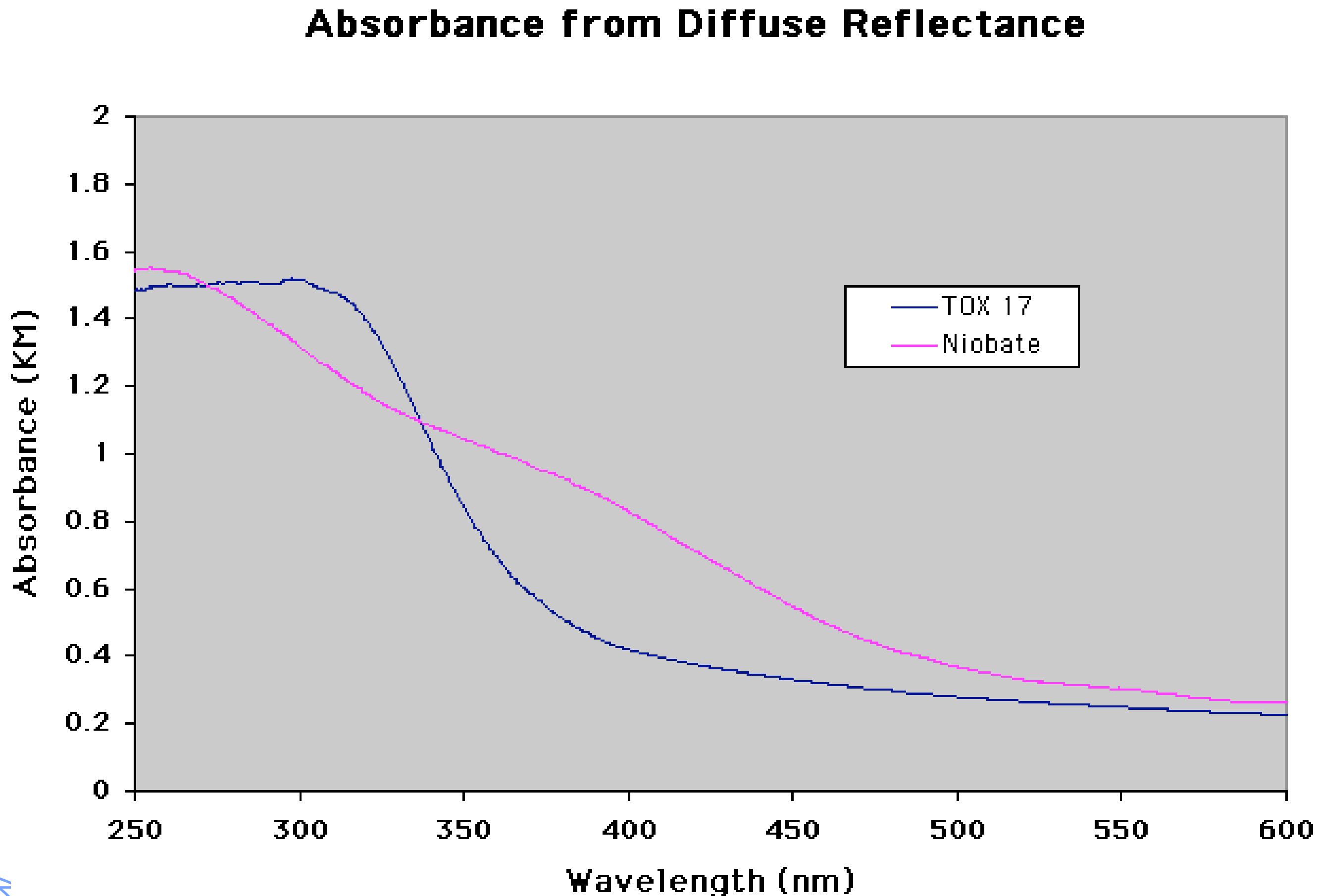
Phase Two

4. Evaluate hydrogen sensor
5. Modeling begun
6. Relocation of NanoGram equipment to SRI
7. Electrochemical analysis module prototype

Accomplishments/Progress (cont.)

Sample	median diameter, μm	uL H_2 / hr m^2 Photo Pt	uL H_2 / hr m^2 IW Pt	uL H_2 / hr m^2 PtRuIrOs
A 25	0.11	27 (3.0)	34 (7.2)	21 (3.8)
A 33	0.10	25 (4.2)	44 (7.3)	23 (5.8)
A 30	0.08	32 (5.9)	56 (9.2)	31 (4.9)
AR 101	0.08	42 (6.4)	63 (10.2)	58 (11.2)
RA 37	0.07	28 (5.8)	36 (8.1)	23 (6.3)
AR 51	0.07	48 (6.2)	64 (11.8)	67 (10.5)
RA 76	0.07	21 (3.9)	24 (5.3)	25 (8.2)
A 50	0.06	38 (7.2)	44 (8.9)	34 (7.3)
A 55	0.06	36 (5.1)	38 (8.4)	31 (7.9)
AR 110	0.06	29 (6.2)	68 (12.9)	71 (13.1)
A 24	0.05	24 (5.8)	32 (7.5)	41 (8.9)
A 57	0.04	33 (7.1)	41 (7.3)	37 (7.4)
AR 113	<0.03	46 (6.4)	69 (14.1)	71 (11.8)
A 82	< 0.03	35 (7.3)	41 (7.5)	33 (6.8)
P25	0.09	21 (6.5)	29 (6.2)	34 (8.3)

Accomplishments/Progress (cont.)



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Accomplishments/Progress (cont.)

Other materials examined with excellent Stability, BUT low activity:

- Indates
  - $Na_{(1-x)}K_xInO_2$
- Niobates
  - $BaNb_{(1-x)}Co_xO_4$
- SiC

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Accomplishments/Progress (cont.)

Ferroelectrics for H_2 production

- Motivation

  Surface nanostructures in La-doped $NaTaO_3$ enhance H_2 production

  Kato *et al*, *J. Am. Chem. Soc*. **125**, 581 (2001)

- Rationale

  Theory: La-doping ⇒ strain & electric field ⇒ macroscopic polarization

  ⇒ domain-wall formation

- Great potential of ferroelectrics in H_2 production

  Minimally explored to date

  Desired charge patterns on surfaces

  Many ferroelectric compounds available

  Tunable properties (band gap, domain-wall size & orientation, etc)

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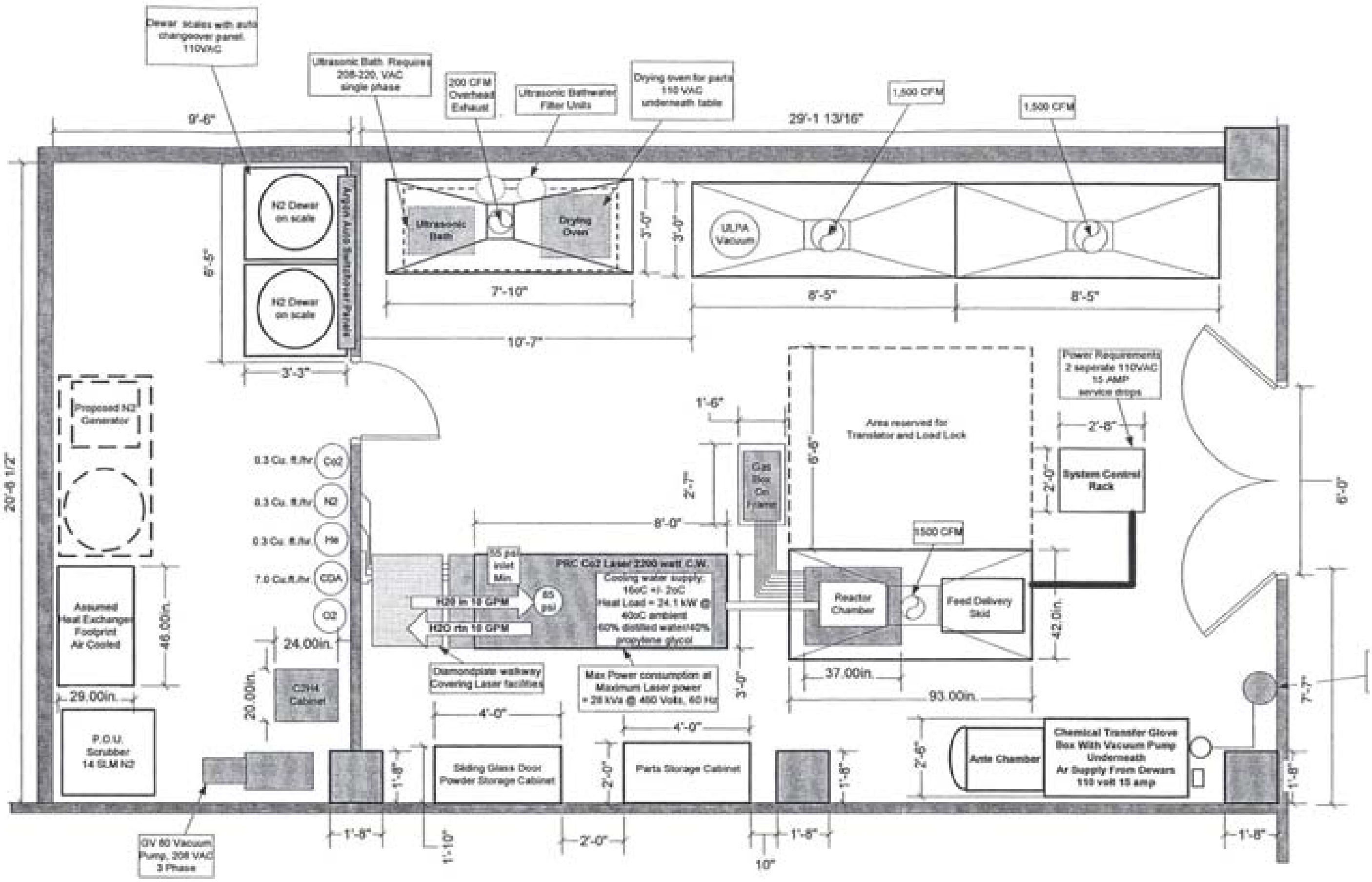
Accomplishments/Progress (cont.)



Interactions/Collaborations

- Presentation at American Ceramics Society, Basic Sciences Division, Oakland CA
- Commercial Clients
- NanoSig
- Materials transfer agreement available

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Detailed Plans for Phase 3

- Task 1 Tools Development
  - **Electrochemistry Analysis Module**
    - **Design review: May 2004**
    - **Fabrication: August 2004**

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Detailed Plans for Phase 3 (cont.)

- Task 2. Analysis of Nanoparticulate-based PEC Systems
  - Analysis and characterization of NanoGram and SRI generated materials
  - Based on results and on modeling develop rationale design of future materials (elemental, phase, size and morphology)
  - Evaluate materials reported in literature
    - Synthesized at SRI
    - Submitted to SRI (Materials Transfer Agreement)

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Detailed Plans for Phase 3 (cont.)

- Task 3. Generation of Database
  - Inclusion of validated data with sufficient information for reproduction in other labs

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Detailed Plans for Phase 3 (cont.)

Task 4 Modeling

- Electronic structure of ferroelectrics

  Large gap (≥ 3.5 eV) in oxide ferroelectrics

  Small gap (< 1 eV) in $Pb_{1-x}Ge_xTe$

  Examine electronic structure for various ferroelectrics and identify systems with desired band gap

- Heterostructures with semiconductor coated by ferroelectric

  Investigate band alignment between the two materials and describe how electron-hole pair created in the semiconductor migrate to the ferroelectric surface

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Reviewers Comments

Communication/Interaction with other groups is lacking.

- Better coordination of efforts with UC-SB, UH, and NREL needs to be established.
- Database to make data available

Material selection needs to be better developed

- Modeling effort will help drive materials selection

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Thank You, Stay Tuned

Slide by R. Smalley Presented at National Nanotechnology Initiative

- **ENERGY**
  is the single most important problem facing humanity today.
- **WE CAN SOLVE THIS PROBLEM**
  with revolutionary breakthroughs at the frontiers of Physical Sciences & Engineering, and particularly in Nanotechnology
- We need a new APOLLO PROJECT to do this.
- The problem is huge, but it is also a magnificent opportunity.
- Success will revolutionize the largest industry in the world, Energy.
- American boys and girls will enter the physical sciences to do this, inspired by their idealism, their sense of mission, and their desire to be "where the action is".
- In the process this new Apollo Project will produce a cornucopia of new technologies, and provide the underpinnings for vast new economic prosperity for the US and the world.

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