II.G.7 Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials

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Objectives

- Continue synthesis and screening of libraries designed in previous years and follow promising (lead) materials as they are identified.
- Perform exploratory design, synthesis and screening of new mixed metal-oxides based on solid solutions and substitutional doping of Zn, W, Fe, and Ti host oxides with the aim of improving the absorption of visible light to an equivalent of a material with a bandgap of approximately 1.7-2.2 eV.
- Explore processing and synthesis parameters to optimize conductivity and minimize charge trapping and surface recombination of materials selected from first two objectives.
- Characterization of the electrocatalytic activity of candidate materials and material coatings to identify and optimize their electrocatalytic properties.
- Continue to investigate the synthesis of libraries of semiconductor heterostructures for improved efficiency and/or stability by creating libraries where heterojunctions will be formed both for passivating otherwise unstable material surfaces (e.g. wide gap oxide on narrow gap material) as well as for utilizing two-photon tandem absorption processes.
- Investigate the theoretical and practical economic potential of alternative surface redox reactions.

- Development of iron oxide thin films based on sol-gel and self assembly methods.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen. Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(Y)   Materials Efficiency

(Z)   Materials Durability

(AA)   PEC Device and System Auxiliary Material

(AB)   Bulk Materials Synthesis

Technical Targets

Characteristics	Units	2003 Target	2006 Target	Achieved 2006	2013 Target
Usable semiconductor bandgap	eV	2.8	2.8	2.2	2.3
Chemical conversion process efficiency (EC)	%	4	4	1	10
Plant solar-to-hydrogen efficiency (STH)	%	NA	NA	NA	8
Plant durability	hr	NA	NA	~100	1,000

Approach

- Systems Development
  - Continuing synthesis and high-throughput screening system upgrades:
    - More samples/higher throughput
    - Faster measurements
    - Increased reproducibility
  - Develop sol-gel chemistry for iron oxide systems.
  - Develop chemistry for iron oxide nanorods growth (self assembly).
- Combinatorial Library Synthesis and Screening
  - Using new and existing high-throughput synthesis and screening technology, create and screen suitable new mixed oxide materials for

electrochemical/photoelectrochemical hydrogen production.

– Catalyze the surfaces and engineer the band-edges of the identified semiconductor materials as required.

– Synthesize, using conventional routes, iron oxide base materials by sol-gel and self assembly of nanorods.

– Determine if existing photovoltaic (PV) device structures could be easily modified to cause the direct splitting of water.

Accomplishments

- Developed a second generation automated system for photoelectrochemical (photocurrent, photovoltage, flat-band potential, action spectra, incident photon conversion to electrons [IPCE]) characterization.

- Explored the synthesis of iron oxide based systems by sol-gel chemistry.

- Developed synthesis conditions for the synthesis of iron oxide nanorods with control over the feature size of the nanorods.

- Synthesis of iron oxide nanorods with efficiencies of ~1% for water splitting and 3% for biomass oxidation to hydrogen and carbon dioxide.

Future Directions

- Electrochemical deposition of iron oxide base systems and selective doping by co-deposition.

- Iron oxide nanorod synthesis and control over growth structure.

- Transition metal doped Fe_2O_3.

- Single-sample slurry reactor for quantitative H_2 analysis.

✧   ✧   ✧   ✧   ✧

Introduction

The overall project objective is to discover and optimize an efficient, practical, and economically sustainable material for photoelectrochemical production of bulk hydrogen from water – a clean, renewable route to hydrogen energy. The properties of the semiconductors investigated for this application, which are similar to those in PV devices, must satisfy conditions in several areas if cost-effective hydrogen production is to be realized: (1) efficient solar absorption, (2) effective charge separation/transport, (3) appropriate conduction band/valence band energies relative to H_2 and O_2 redox potentials ("band matching"), (4) facile interfacial charge transfer,

(5) long-term stability, and (6) low cost. A material which satisfies all the above conditions simultaneously could provide clean hydrogen in bulk and at low cost; unfortunately, no such material or system has been discovered or developed to date. The DOE has identified the following future targets for solar-to-hydrogen efficiency and durability: 2013, 8% and 1,000 hrs; 2018, 10% and 5,000 hrs.

Hematite (α-Fe_2O_3) has many potential advantages for hydrogen photoproduction. It has a bandgap of 2-2.2 eV (absorbs approximately 40% of the solar spectrum), it is stable in electrolytes over a wide range of pHs and is abundant, inexpensive and non toxic [1-3]. Several qualities have limited the use of this material as an efficient photocatalyst, including high electrical resistance and recombination rates of photogenerated electrons [4,5] and conduction band that is lower than the redox level of H^+/H_2. The undesirable electrical properties are partially due to the hopping mechanism of charge transfer via oxygen vacancies, grain boundaries, and surface traps, which results in relatively low quantum yields, while the low conduction band is due to the Fe 3d electrons. Efforts have been devoted to reducing the resistivity of thin films by increasing the amount of charge carriers or transferring electrons along the (001) planes of the hematite, which has four orders of magnitude lower resistance than transport perpendicular to this plane. This last approach combined with Si doping has already shown some improvement of the hematite [6,7], however, there is still much work to be done to increase the record IPCE (400 nm) of 42%. Our hypothesis is that by deliberately doping hematite with selected heteroatoms, and being able to control the growth dimensions, crystal orientation and facets, these limitations may be overcome. There is much diversity to explore in searching for the appropriate combination of dopant species to improve photocatalytic performance [5,8-10] as well as to understand and engineer the crystal structure, orientation and size of the crystalline domains of hematite.

Approach

The approach of this project involves the application of combinatorial chemistry methods to discover and optimize photoelectrochemical materials and systems for cost-effective hydrogen production. This represents a shift in the research paradigm from conventional chemical research in that a combinatorial approach that features systematic and high-speed exploration of new metal-oxide based solid-state materials. By investigating large arrays of diverse materials, we are working to improve the understanding of the fundamental mechanisms and composition-structure-property relationships within these systems while discovering new and useful energy-producing photocatalysts. It should also be noted that our approach focuses upon

the investigation of semiconductor materials that are inherently inexpensive, such as iron oxide for example. Iron oxide materials can be synthesized by rapid serial electrodeposition techniques or can be synthesized by sol-gel or self assembly of nanorods, which are a single sample technique. However, the limiting step in this case is still the high throughput screening of materials. Thus by utilizing the high throughput screening system we can expedite the material discovery.

Results

We have redesigned our automated screening system to perform zero bias photocurrent, current-voltage (IV) curves and photovoltage measurements in the same scan, therefore decreasing the total time needed for the measurements by ~40%. A sketch showing the high throughput photoelectrochemical system is shown in Figure 1.

Iron oxide has been synthesized by sol-gel techniques. Results indicate that doping is achievable by sol-gel techniques. Several dopants such as Cu, Ti, Mg, Zn, and W were investigated. Titanium showed the most promising results showing an order of magnitude improvement of the photocurrent versus that of the undoped materials (Figure 2a). The ratio of the photocurrent under full spectrum illumination (ultra-violet [UV]+visible light [VIS])/VIS shows that the addition of titanium atoms don't contribute to the UV photocurrent which would be expected if the titanium atoms were phase segregated and would form a TiO_2 region inside the Fe_2O_3 matrix. Under applied bias the performance of the samples was improved by 200% (Figure 2b). Although this is a great improvement compared to the undoped samples, sol-gel synthesized iron oxide showed extremely poor performance (>0.5% efficiency) and the synthesis of iron oxide based materials by this method was terminated.
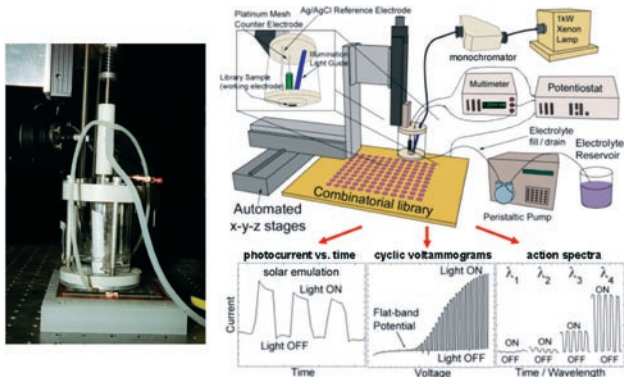

FIGURE 1. Automated Photoelectrochemical Screening (A unique photoelectrochemical probe is stepped across the library, analyzing one sample at a time in automated fashion, measuring photocurrent, photovoltage, cyclic voltammograms, action spectra, etc.)
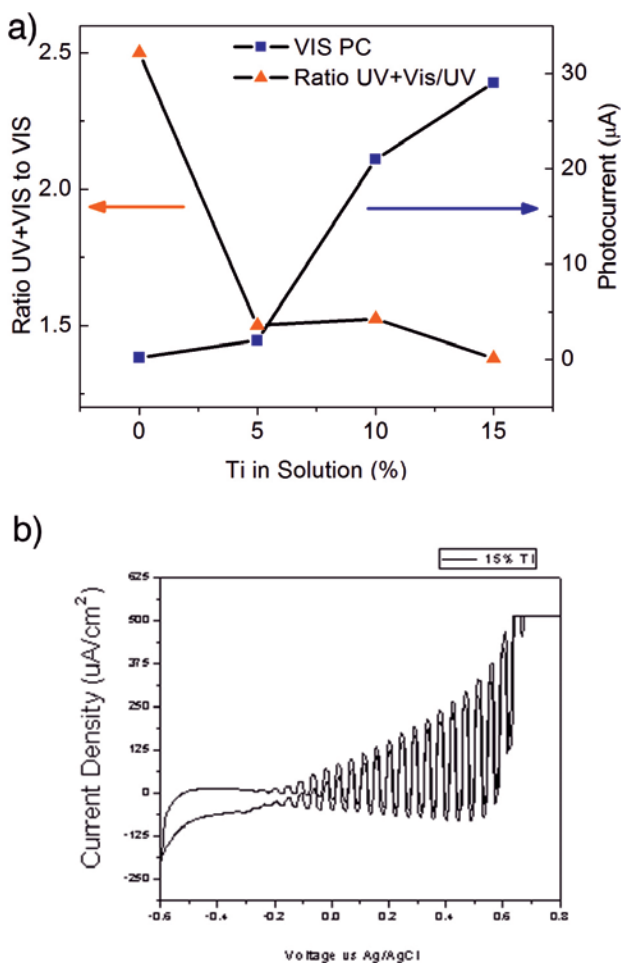

FIGURE 2. a) (UV+VIS light/VIS light) Ratio and Photocurrent versus Percent of Titanium Atoms in Fe_2O_3 Sol-Gel Sample; b) IV Characteristics of 15% Ti Sample

Iron oxide nanorods are now being grown by modifying the recipe of Vayssieres [6] to investigate the synthesis condition and be able to control the crystalline orientation of the nanorods with respect to the substrate as well as the size and aspect ratio of the nanorods. Figure 3 shows that the size of the nanorods can be controlled by changes in the growth parameters. Figure 4 shows the UV-VIS spectra of the nanorods; from this figure we can see that the optical bangap remains unchanged while the absorption of the
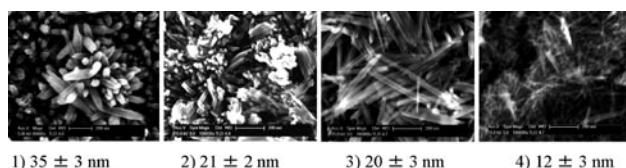

1) 35 ± 3 nm   2) 21 ± 2 nm   3) 20 ± 3 nm   4) 12 ± 3 nm

FIGURE 3. Scanning Electron Micrographs of Different Growth Conditions of Nanorods (The average diameter of the nanorods is shown at the bottom.)
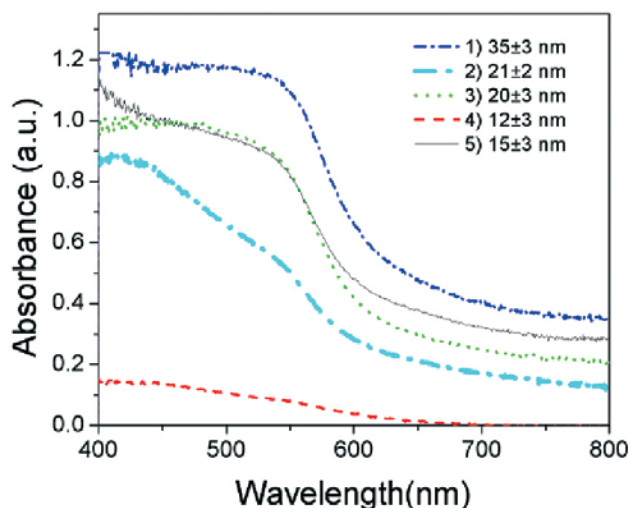
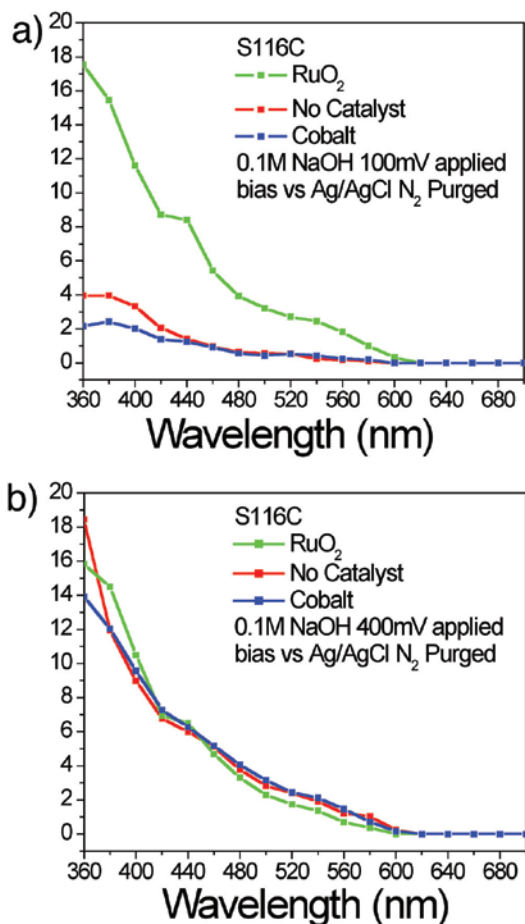**FIGURE 4.** UV-VIS Absorption of the Nanorod Samples

FIGURE 5. (a, b) IPCE of 35 nm Fe_2O_3 nanorods with an applied bias of 100 mV and 400 mV, showing the dramatic improvement of the nanorods with the electrodeposition of RuO_2 at low applied bias while at high applied bias the oxygen evolution catalyst is not improving the performance of the nanorods.

sample is dependant on the size, packing fraction and thickness of the nanorods (variables which are not fully characterized). IPCE of a nanorod sample (Figure 5) shows that the under a low applied bias (100 mv vs Ag/AgCl) the photoelectrochemical performance is limited by the oxygen evolution reaction in which RuO_2 serves as a good catalyst and shows an IPCE of ~18 vs. 4% for the samples with no surface catalyst. At higher applied bias (Figure 5b) there is almost no difference between the samples with or without RuO_2, however a higher efficiency is observed with RuO_2 at a low applied bias as shown in the table in Figure 6b. Figure 6a shows the IV curve of different size nanorods showing an efficiency of ~1% at 300 mV.

Conclusions

- The best performing iron oxide sol-gel samples are those doped with titanium at 10-15% atomic ratio.
- Iron oxide nanorods have shown superior performance over that of iron-oxide synthesized by sol gel.
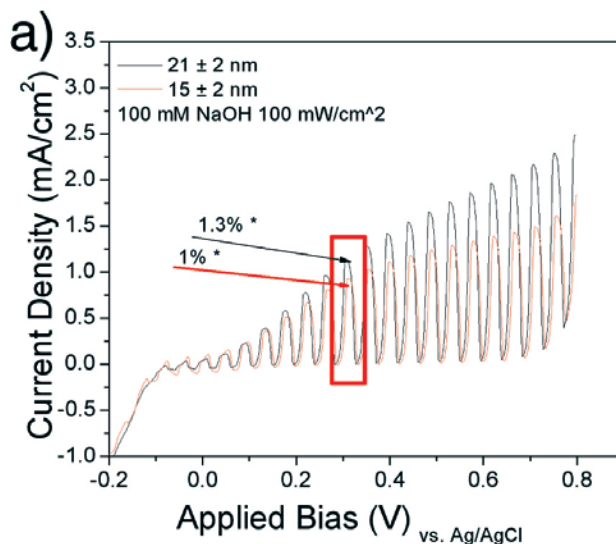
Applied Bias		
	100 mV	400 mV
No Catalyst	0.3%	1.0%
RuO_2	1.6%	0.9%
Cobalt	0.2%	1.0%

FIGURE 6. a) Photoelectrochemical performance of 21 and 15 nm nanorods under applied bias showing efficiency of 1.3% and 1% respectively. b) Table of results showing the efficiency of the nanorods from Figures 2 and 3.

- The oxygen evolution reaction has been identified as one hurdle in the photoelectrochemical production of hydrogen. Several routes for depositing catalyst are being developed such that the electrocatalyst size is consistent with that of the overall system.
- Iron oxide nanorods have been synthesized with variation on the size of the nanorod diameter and aspect ratio. Further work in this area is required to fully understand the growth mechanism and be able to achieve tighter control over the crucial dimensions of the nanorods.

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