An Integrated Approach for Hydrogen Production and Storage in Complex Hydrides of Transitional Elements

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University of Arkansas at Little Rock
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Project ID #
STP19

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Overview

Timeline
- Start: July 2006
- End: August 2009
- Percent complete 10%

Barriers
- Barriers addressed
  - (AP) Materials Efficiency
  - (AS) Device Configuration Designs
  - (P) Lack of understanding of Hydrogen Physisorption & chemisorption

Budget
- Total project funding $
  - DOE share $890,998
  - Contractor share $381,543
- Funding received in FY06 $890,998

Partners
- Interactions/ collaborations
  1. National Institute for Isotopic & Molecular Technologies, Romania
  2. Arkansas NanoTech Center, Little Rock
## Objectives

| Overall | • Optimize Electrolysis and Photoelectrolysis for generation of hydrogen for fuel cells \( (H_2 \text{ production}) \)  
|         | • Develop the materials for hydrogen storage based on DOE’s system storage targets \( (H_2 \text{ storage}) \) |
| 2006-07 | • Setting up energy research laboratory  
|         | • Develop cost-effective semiconductor nanocrystalline electrodes for dye sensitized solar cells \( (H_2 \text{ production}) \)  
|         | • Metal Hydride / Storage Materials screening \( (H_2 \text{ storage}) \) |
Objectives

• Generation of Hydrogen (H₂ production)
  – Develop and study new designs for the optimization of the electrolysis based hydrogen generation process.
  – Optimization of photo-electrolysis reactors to increase their durability and reduce the cost of hydrogen generation
  – Development of cost effective materials for the electrodes of the PEC cells
  – Use surface alteration methods to improve the functionality of the materials used in the PEC cells.
  – Develop outreach and educational programs

• Develop materials for hydrogen storage based on DOE’s system storage target (H₂ storage)
  – Develop nanostructural based materials for hydrogen uptake that have the potential to meet the DOE goals of 7.5%. These storage systems are envisioned to be more compact, lighter in weight, and efficient.
  – Study solid state nanostructural systems that can reversibly absorb hydrogen at higher densities and improved kinetics.
  – Understand the interaction between gaseous hydrogen and these systems
  – Develop outreach and educational programs
Approach

• **H₂ production**
  – Utilizing Photovoltaic energy for water electrolysis
    • Dye sensitized solar cell as a cost effective method for generating photovoltaic energy
    • Triple junction solar cell for photovoltaic energy
  – Photoelectrochemical processes for H₂ generation
    • Bandgap matching between semiconductor materials and solar radiation
      – Plasma surface modification
      – Doping with carbon nanotubes
Approach

• **H₂ Storage**
  – Nanostructural Materials
  – Magnesium and Magnesium Alloy Hydrides
  – Group III Hydride Complexes
  – Growth and characterization of Nanostructured Metal Hydrides using Oblique Angle Deposition
SIGNIFICANT ACCOMPLISHMENTS

- Preliminary studies done on plasma surface modification of nanocrystalline TiO$_2$
- Hydrogen storage characterization system designed and fabrication underway
- Candidate storage materials identified for screening
- Preliminary studies on Pd/carbon nanofibers uptake system
- Oblique angle deposition system set up and nanostructures of Magnesium fabricated
ACCOMPLISHMENTS

H₂ Production

- A Dye sensitized solar cell has been fabricated.
- A photoelectrochemical cell is under construction.
- Plasma surface modification of nanocrystalline TiO₂.

  - 5 nm diameter TiO₂ nanoparticles were obtained from Nanostructured & Amorphous Materials, Inc.
  - Atmospheric pressure dielectric barrier discharge plasma reactor made of a cylindrical Pyrex glass tube (30 mm inner diameter, 90 cm long) with a pair of copper electrodes (7.5 cm x 3 cm) placed across the reactor.
  - The capacitively coupled plasma generator was operated at a frequency of 700 Hz. The voltage across the electrodes was 12 kVrms. The sample was placed in a glass boat between the electrodes and He was injected from the inlet of the reactor.
  - The samples were exposed to plasma for 10 minutes.
ACCOMPLISHMENTS

H$_2$ Production

Atmospheric-pressure Helium Plasma used for Surface Modification of nanocrystalline TiO$_2$
Preliminary data shows that plasma surface modification increased the surface area of nanocrystalline TiO\textsubscript{2} particles. Surface area was measured using Micromeritics ASAP 2020 Surface Area analyzer.
**H₂ Production**

**ACCOMPLISHMENTS**

BET Surface area of TiO₂ nanoparticles

![Graph showing BET Surface area for different treatments](chart.png)

- **As is**: Surface area (m²/g) 136
- **Heat treatment**: Surface area (m²/g) 134
- **Plasma treatment**: Surface area (m²/g) 142
- **Plasma + heat treatment**: Surface area (m²/g) 138

**H₂ Production ACCOMPLISHMENTS**

BET Surface area of TiO₂ nanoparticles

![Graph showing BET Surface area for different treatments](chart.png)

- **As is**: Surface area (m²/g) 136
- **Heat treatment**: Surface area (m²/g) 134
- **Plasma treatment**: Surface area (m²/g) 142
- **Plasma + heat treatment**: Surface area (m²/g) 138
H₂ Production

ACCOMPLISHMENTS

Average Pore diameter of TiO₂ nanoparticles

<table>
<thead>
<tr>
<th>Treatment</th>
<th>BJH Adsorption average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As is</td>
<td>111.2</td>
</tr>
<tr>
<td>Heat treatment</td>
<td>117.6</td>
</tr>
<tr>
<td>Plasma treatment</td>
<td>113.4</td>
</tr>
<tr>
<td>Plasma + heat treatment</td>
<td>116.3</td>
</tr>
</tbody>
</table>
H₂ Production  

ACCOMPLISHMENTS

Adsorption isotherm for TiO₂ nanoparticles

Isotherm Linear Plot

- TiO₂ 5nm - Adsorption
- TiO₂ 5nm - Desorption

Quantity Adsorbed (mmol/g)

Relative Pressure (p/p°)
H₂ Production

ACCOMPLISHMENTS

Adsorption isotherm for plasma treated TiO₂ nanoparticles

Isotherm Linear Plot

TiO₂ 5nm Plasma - Adsorption
TiO₂ 5nm Plasma - Desorption
H₂ Storage

ACCOMPLISHMENTS
Pressure Based Quantitative Hydrogen Absorption Measurement Instrument (Sievert Apparatus)

I. Sample Chamber
II. Reference Volume
III. Ohmic Heating Elements
IV. Thermocouples
V. Flow Control Conduit
VI. Pressure Transducers
VII. Solenoid Valve Actuator
VIII. Manual Valves

Vacuum

H₂ Cylinder
### H₂ Storage

#### ACCOMPLISHMENTS

**Measurement Instrument Operational Ranges and Resolutions**

- Pressure Measurement Range: \(0 \rightarrow 200\) Atm
- Thermal Operating Range: \(-20 \rightarrow 450\) °C

<table>
<thead>
<tr>
<th>Pressure Range</th>
<th>Temperature</th>
<th>Pressure Resolution</th>
<th>Hydrogen Mass Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 10 Atm</td>
<td>0 °C</td>
<td>0.01 Atm</td>
<td>4.5 x 10^{-5} g H₂</td>
</tr>
<tr>
<td>0 – 10 Atm</td>
<td>100 °C</td>
<td>0.01 Atm</td>
<td>3.3 x 10^{-5} g H₂</td>
</tr>
<tr>
<td>0 – 10 Atm</td>
<td>400 °C</td>
<td>0.01 Atm</td>
<td>1.8 x 10^{-5} g H₂</td>
</tr>
<tr>
<td>10 – 65 Atm</td>
<td>0 °C</td>
<td>0.065 Atm</td>
<td>2.7 x 10^{-4} g H₂</td>
</tr>
<tr>
<td>10 – 65 Atm</td>
<td>100 °C</td>
<td>0.065 Atm</td>
<td>1.9 x 10^{-4} g H₂</td>
</tr>
<tr>
<td>10 – 65 Atm</td>
<td>400 °C</td>
<td>0.065 Atm</td>
<td>1.0 x 10^{-4} g H₂</td>
</tr>
<tr>
<td>65 – 200 Atm</td>
<td>0 °C</td>
<td>0.2 Atm</td>
<td>8.9 x 10^{-4} g H₂</td>
</tr>
<tr>
<td>65 – 200 Atm</td>
<td>100 °C</td>
<td>0.2 Atm</td>
<td>6.5 x 10^{-4} g H₂</td>
</tr>
<tr>
<td>65 – 200 Atm</td>
<td>400 °C</td>
<td>0.2 Atm</td>
<td>3.6 x 10^{-4} g H₂</td>
</tr>
</tbody>
</table>
# H₂ Storage

## ACHIEVEMENTS (CANDIDATE STORAGE MATERIALS)

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Examples</th>
<th>Advantages</th>
<th>Difficulties</th>
<th>Solution Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nanostructural Materials</strong></td>
<td>• Carbon Nanotubes</td>
<td>• Reasonable Adsorption kinetics</td>
<td>• Adsorption process requires cryogenic temperatures</td>
<td>• Application of Hydrogen Dissociation Catalysts to Increase Adsorption Temperatures</td>
</tr>
<tr>
<td></td>
<td>• Amorphous Carbon</td>
<td>• Desorption is easily thermally reversible</td>
<td>• Samples can be inconsistent</td>
<td>• Modify production techniques to increase surface area and quality</td>
</tr>
<tr>
<td></td>
<td>• Carbon Nanofibers</td>
<td></td>
<td>• Lower percent mass Hydrogen storage ~(.5% - 5%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Metal Organic Frameworks</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Nanorods</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Magnesium and Magnesium Alloy Hydrides</strong></td>
<td>(percent mass)</td>
<td>• Higher percent mass Hydrogen storage ~(2.5%-7.5%)</td>
<td>• Hydride formation decomposition typically involves high temperatures (~400 °C)</td>
<td>• Substitution of new alloy metals</td>
</tr>
<tr>
<td></td>
<td>• Mg-(10)Al</td>
<td>• Can easily be mass produced</td>
<td>• Can sometimes require high pressures</td>
<td>• Introduction of catalytic compounds</td>
</tr>
<tr>
<td></td>
<td>• Mg-(25)Ni</td>
<td>• Can have practical absorption and desorption kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Group III Hydride Complexes</strong></td>
<td>• Li[AlH₄]</td>
<td>• Very High Storage Capacity</td>
<td>• Direct hydride formation can be difficult</td>
<td>• Use of intermediate reactions or catalyst to lower formation and decomposition temperatures and pressures</td>
</tr>
<tr>
<td></td>
<td>• Na[AlH₄]</td>
<td>• Compounds range from ~7.5% to ~18.5% Hydrogen by mass</td>
<td>• Covalent hydride gasses may form (e.g. B₂H₆)</td>
<td>• Development of filters or chemical compounds to eliminate covalent hydride gas</td>
</tr>
<tr>
<td></td>
<td>• K[BH₄]</td>
<td>• Stable if dry</td>
<td>• Decomposition typically occurs at high temperatures</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Na[BH₄]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**H₂ Storage ACCOMPLISHMENTS (CANDIDATE STORAGE MATERIALS)**

**Examples**

- Carbon Nanotubes
- Amorphous Carbon
- Carbon Nanofibers
- Metal Organic Frameworks
- Nanorods

**Advantages**

- Reasonable Adsorption kinetics
- Desorption is easily thermally reversible

**Difficulties**

- Adsorption process requires cryogenic temperatures
- Samples can be inconsistent
- Lower percent mass Hydrogen storage ~(.5% - 5%)

**Solution Approach**

- Application of Hydrogen Dissociation Catalysts to Increase Adsorption Temperatures
- Modify production techniques to increase surface area and quality

- Substitution of new alloy metals
- Introduction of catalytic compounds

**Group III Hydride Complexes**

- Li[AlH₄]
- Na[AlH₄]
- K[BH₄]
- Na[BH₄]

**Advantages**

- Very High Storage Capacity
- Compounds range from ~7.5% to ~18.5% Hydrogen by mass
- Stable if dry

**Difficulties**

- Direct hydride formation can be difficult
- Covalent hydride gasses may form (e.g. B₂H₆)
- Decomposition typically occurs at high temperatures

**Solution Approach**

- Use of intermediate reactions or catalyst to lower formation and decomposition temperatures and pressures
- Development of filters or chemical compounds to eliminate covalent hydride gas
Pd/Carbon Nanofibers uptake system

- Pd nanoparticles – carbon nanofibers mixtures were prepared using a Pd/La₂O₃ catalyst by Chemical Vapor Deposition.
- Their hydrogen uptake properties were analyzed and compared with those of the purified carbon nanotubes samples.
- Pd has a high potential as a by-pass transfer of hydrogen to the carbon nanostructures and to supply atomic hydrogen at the Pd-carbon interface.

Raman Spectroscopy indicated the presence of all the bands corresponding to Carbon nanostructures:

- D band at 1326 cm⁻¹
- G band at 1588.1 cm⁻¹
- 2D band at 2651.9 cm⁻¹
H₂ Storage

Pd/Carbon Nanofibers uptake system

- Hydrogen uptake experimental results show saturation at 1.5 wt. % of the hydrogen adsorbed on the carbon nanofibers’ surface.

- There was found a direct correlation between the amount of adsorbed hydrogen and the Pd/C ratio. Basically, an increase in the amount of metallic Pd corresponds to a higher hydrogen adsorption value on the carbon nanofibers.

- These results can be explained by:
  - the catalytic properties of the Pd particles that dissociate H₂ into atomic H.
  - the possible charge transfer between Pd and C, given the work function difference between palladium (5.1-5.6 eV) and carbon nanofibers (4.9-5.05 eV). The relationship between the H uptake values by the C nanofibers and the Pd/C ratio shows that the atomic H that is generated by Pd diffused on the C surface, but not at very large distances.
  - the H uptake values vary with the contact surface area between the Pd nanoparticles and the C nanofibers.
Nanostructured Metal Hydrides for Hydrogen Storage

Fabrication technique: **Oblique angle deposition**

Some examples of nanostructures grown by oblique angle deposition (made of Si, RPI, 2005):


Reviews:
Advantages of Oblique Angle Deposition

• **Simple, cheap, & effective**: 3D nanostructures through physical self-assembly
• Structures that are **not possible** to produce by *lithographical* techniques (e.g. springs, slanted rods, balls)
• Almost **no materials limit** for the nanostructures made of (many of the elemental materials in the periodic table)
• Can be grown on almost **any substrate** material
• Control of nanostructure **size and separation** (tens–hundreds of nm)
• **Novel** material properties

Motivation

*Obliquely deposited nanorods and nanosprings of metal hydrides are expected to provide superior hydrogen storage properties* because of:

- **Large surface area to volume ratio**: Due to the large surface area and small diameters of the nanostructured metal hydrides, the rate of absorption and desorption will be faster.
- **Crystal orientation** of the structures can be optimized through the deposition parameters of GLAD for the maximum hydrogen absorption/desorption rates.
- Due to the **lower oxidation rate** of single crystal GLAD nanostructures, hydrogen permeability will be further enhanced.
- Porous structure will improve the **mechanical elasticity** of the metal hydride system that might be needed during possible volumetric changes due to the absorption/desorption of hydrogen.
H₂ Storage

ACCOMPLISHMENTS
Progress and Results

• Set-up of a Oblique Angle Sputter Deposition System:

  • DC/RF power supply capability
  • Computerized substrate tilt and rotation control
  • Sample sizes up to about 5cmx5cm
  • Installation has been finished in February 2007
## H₂ Storage

- Growth and physical characterization magnesium (Mg) nanostructures for hydrogen storage

#### Morphology and Microstructure: High surface to volume ratio for nanostructured Mg

Nanostructured Mg by oblique angle deposition

Conventional smooth Mg thin film by normal angle deposition

**Deposition Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nanostructured Mg (ID030407_1)</th>
<th>Conventional Mg thin film (ID030607_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition Angle</td>
<td>85 °</td>
<td>0 °</td>
</tr>
<tr>
<td>Substrate Rotation speed</td>
<td>5 RPM</td>
<td>1 RPM</td>
</tr>
<tr>
<td>DC Power</td>
<td>100 Watts</td>
<td>100 Watts</td>
</tr>
<tr>
<td>Deposition Time</td>
<td>60 mins</td>
<td>37 mins</td>
</tr>
<tr>
<td>Base Pressure</td>
<td>2.4*10⁻⁷ mbar</td>
<td>3.1*10⁻⁷ mbar</td>
</tr>
<tr>
<td>Ar Pressure</td>
<td>3.0*10⁻³ mbar</td>
<td>3.0*10⁻³ mbar</td>
</tr>
<tr>
<td>MFC</td>
<td>2.9 ccm</td>
<td>3.1 ccm</td>
</tr>
<tr>
<td>Film Thickness</td>
<td>~1 μm</td>
<td>~1 μm</td>
</tr>
</tbody>
</table>

#### Effective Surface Area: About 90 times larger for the nanostructured Mg film above compared to the conventional Mg thin film of a similar thickness (~1 μm)
Crystal Orientation (Texture):
- Development of (101) texture in nanostructured Mg films while conventional Mg films is highly (002) oriented: (101) oriented nanostructures is likely to have different H2 absorption/desorption kinetics compared to (002) oriented thin films.
- No oxidation peaks have been observed
Summary

• A dye sensitized solar cell was designed and fabricated; *(H₂ production)*

• Plasma surface was employed for surface modification of nanocrystalline TiO₂ used as an electrode in Photoelectrochemical cell; *(H₂ production)*

• A novel oblique angle sputter deposition technique in order to grow nanostructured Mg films for hydrogen storage applications was utilized; *(H₂ storage)*

• Initial results show that Mg nanostructures have high surface to volume ratios apparent with superior effective surface area values; *(H₂ storage)*

• Crystal orientation of Mg nanostructures are also quite different than the conventional thin films of Mg; *(H₂ storage)*

• No significant oxidation has been observed in our nanostructured films *(H₂ storage)*
Future Work

• Doping nanocrystalline TiO$_2$ for bandgap matching; (**$H_2$ production**)

• Electrochemical film deposition for Photoelectrochemical hydrogen generation; (**$H_2$ production**)

• Growth of nanostructured Mg in the shapes of rods and springs, and investigation of their physical and hydrogen absorption properties; (**$H_2$ storage**)

• Growth of Mg nanostructures on patterned substrates for further control on size, shape, and separation; (**$H_2$ storage**)

• Incorporation of catalysis impurities into the Mg nanostructures through the use of custom made sputter sources in order to further enhance the hydrogen absorption/desorption kinetics. (**$H_2$ storage**)