UNIVERSITY
OF ARKANSAS
AT LITTLE ROCK

DOE Hydrogen Program

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

Overview

Timeline

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

Budget

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

Barriers

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

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 production**) •Develop the materials for hydrogen storage based on DOE's system storage targets (**H_2 storage**)
2006-07	•Setting up energy research laboratory •Develop cost-effective semiconductor nanocrystalline electrodes for dye sensitized solar cells (**H_2 production**) •Metal Hydride / Storage Materials screening (**H_2 storage**)

Objectives

- Generation of Hydrogen (**H_2 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 (**H_2 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 al at higher densities and improved kinetics.
  - Understand the interaction between gaseous hydrogen and these systems
  - Develop outreach and educational programs

Approach

- H_2 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 H_2 generation
    - Bandgap matching between semiconductor materials and solar radiation
      - Plasma surface modification
      - Doping with carbon nanotubes

Approach

- **H_2 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

H_2 Production

- **A Dye sensitized solar cell has been fabricated.**
- **A photoelectrochemical cell is under construction.**
- **Plasma surface modification of nanocrystalline TiO_2.**
  - 5 nm diameter TiO_2 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

ACCOMPLISHMENTS

H_2 Production

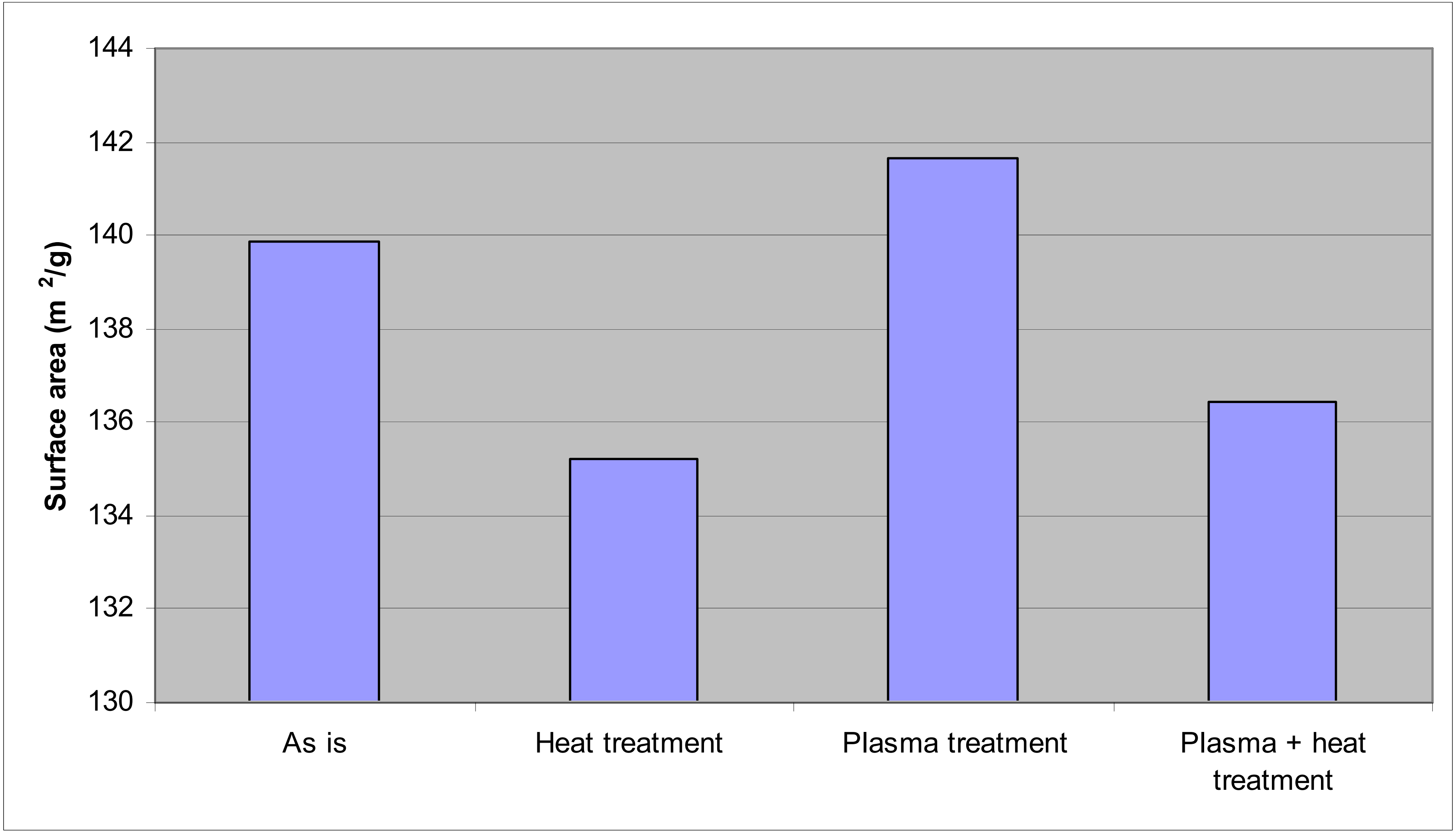
Surface Area analysis

- Preliminary data shows that plasma surface modification increased the surface area of nanocrystalline TiO_2 particles.

Surface area was measured using Micromeritics ASAP 2020 Surface Area analyzer

H_2 Production **ACCOMPLISHMENTS**

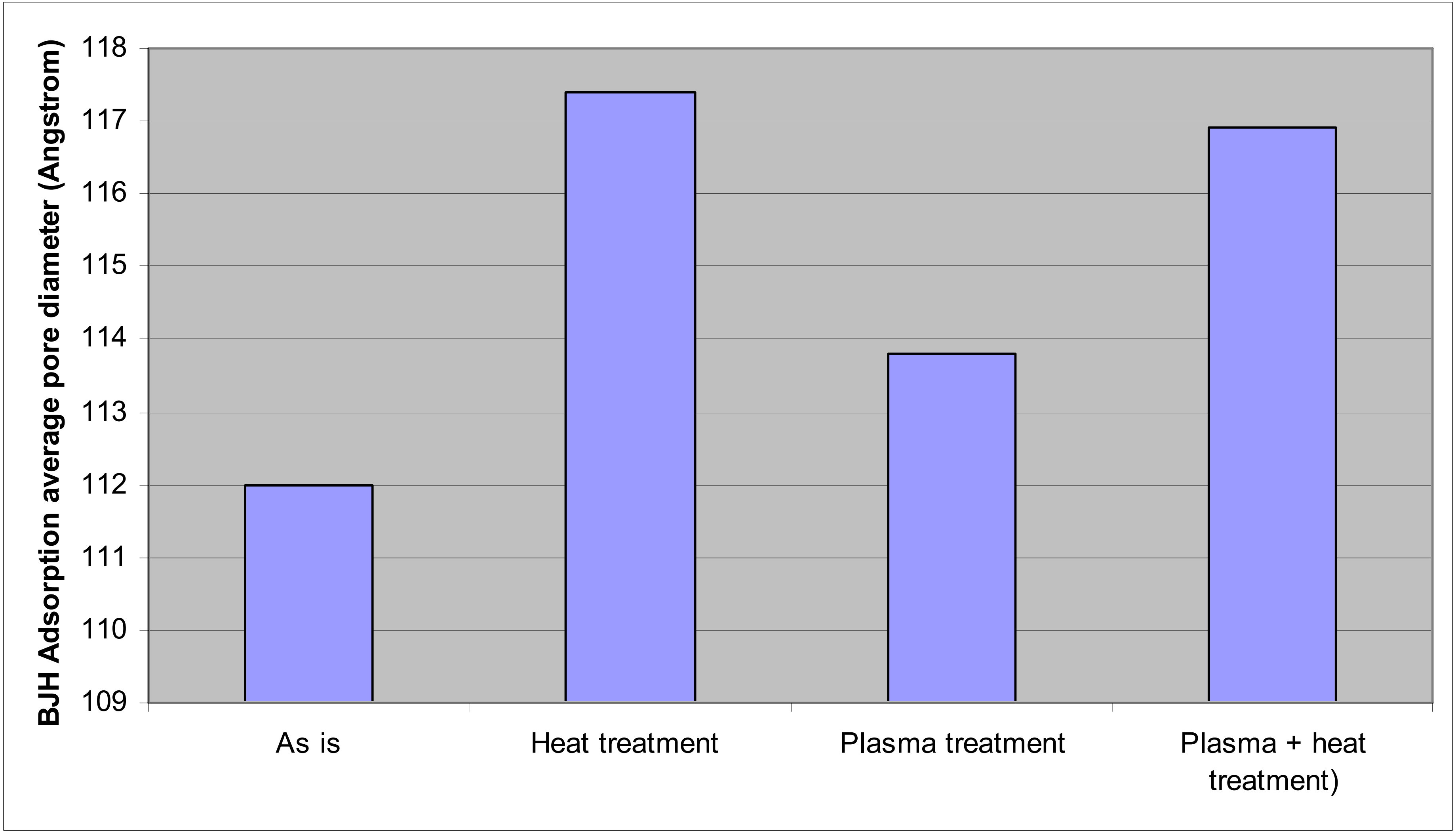
BET Surface area of TiO_2 nanoparticles



H_2 Production

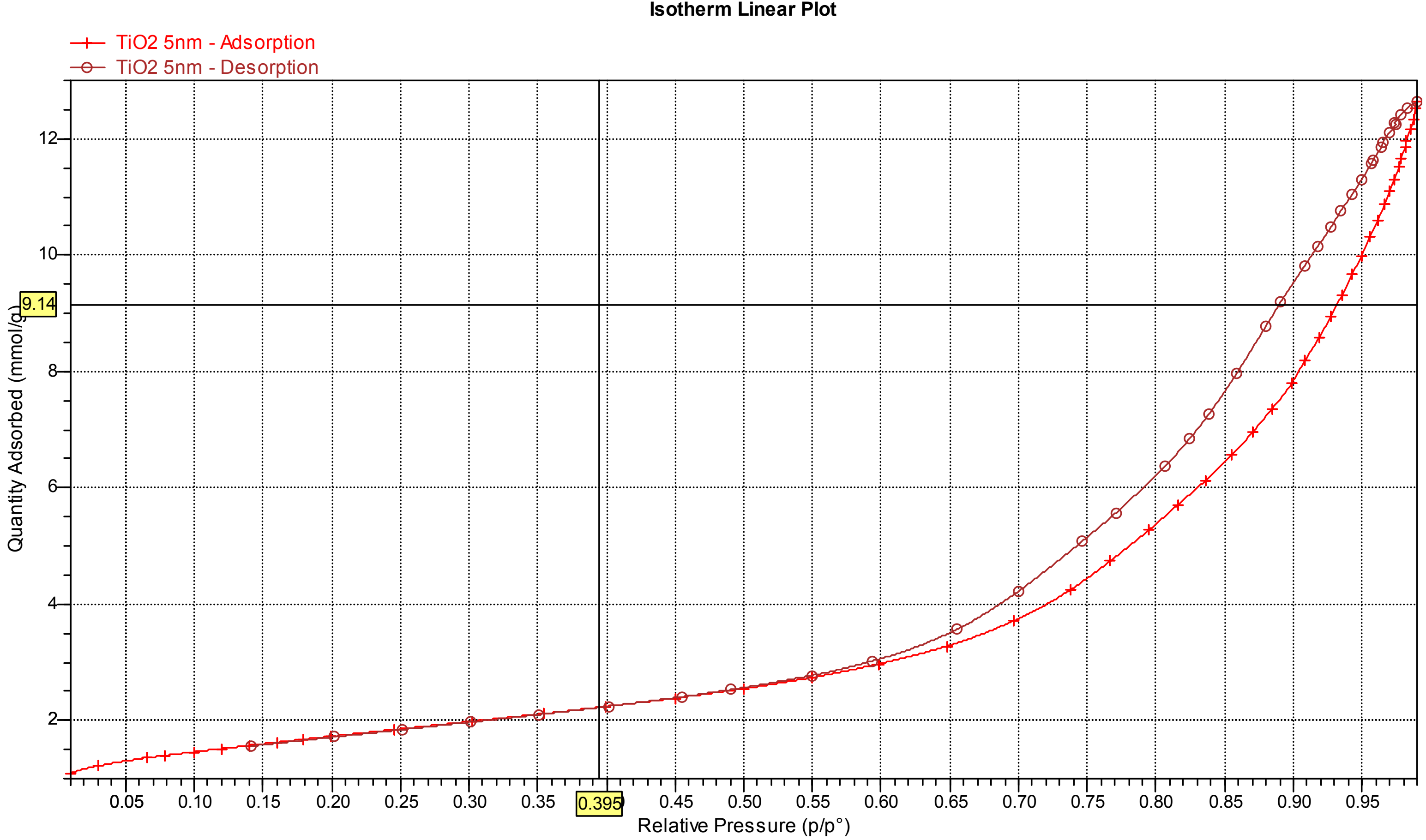
ACCOMPLISHMENTS

Average Pore diameter of TiO_2 nanoparticles



H_2 Production **ACCOMPLISHMENTS**

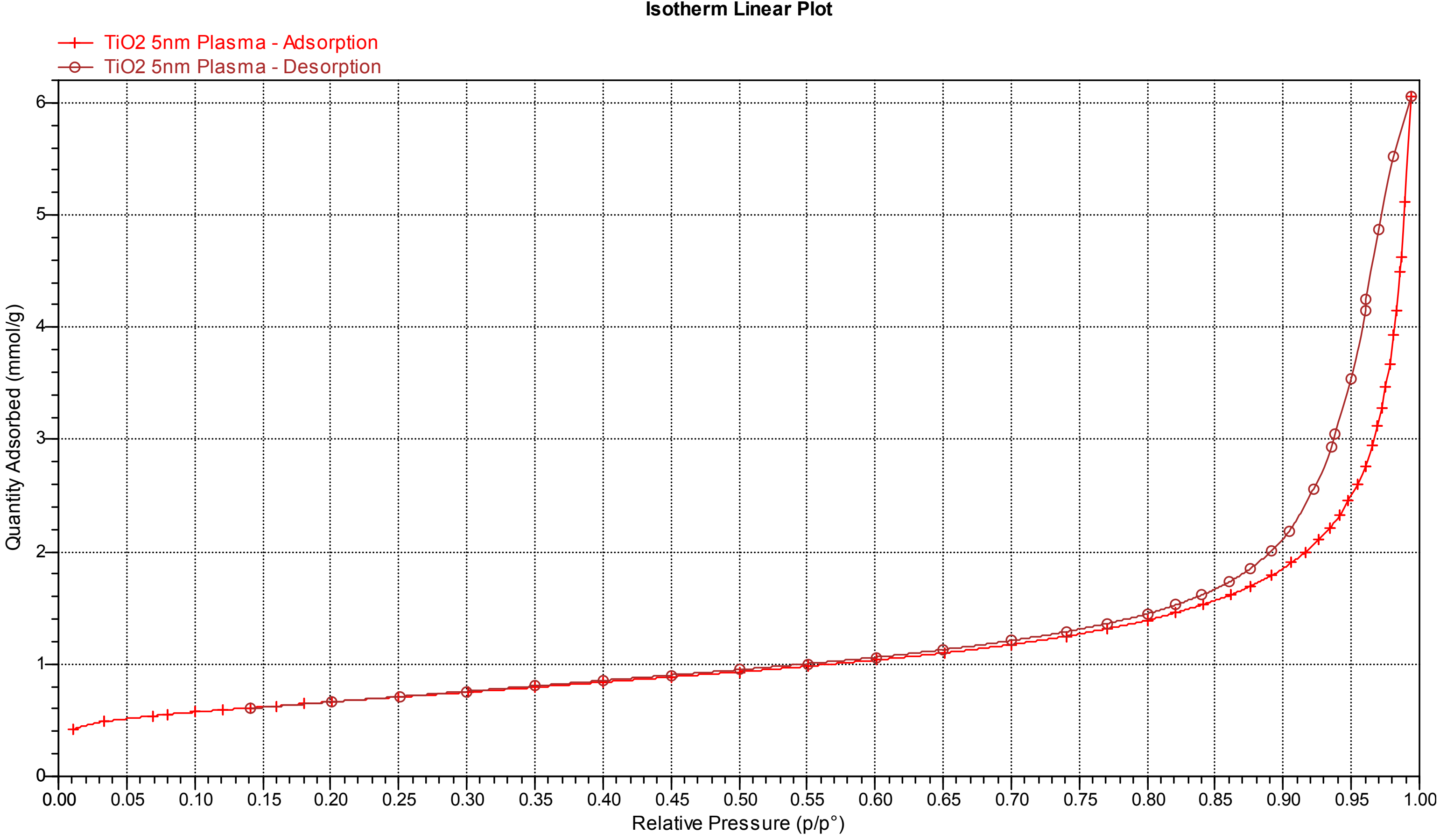
Adsorption isotherm for TiO_2 nanoparticles



H_2 Production

ACCOMPLISHMENTS

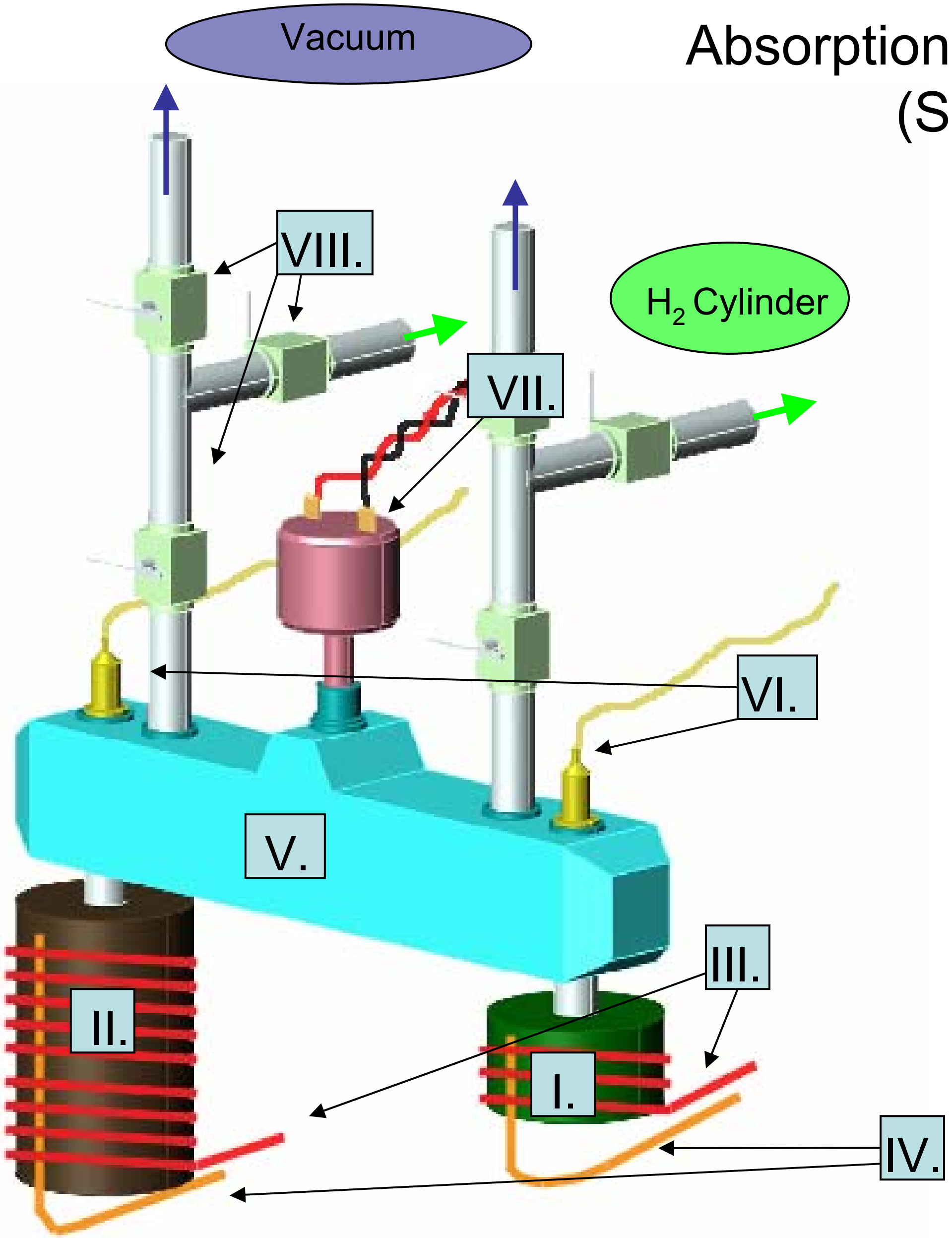
Adsorption isotherm for plasma treated TiO_2 nanoparticles



H$_2$ 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

ACCOMPLISHMENTS

Measurement Instrument Operational Ranges and Resolutions

- Pressure Measurement Range: 0 → 200 Atm
- Thermal Operating Range: -20 → 450 °C

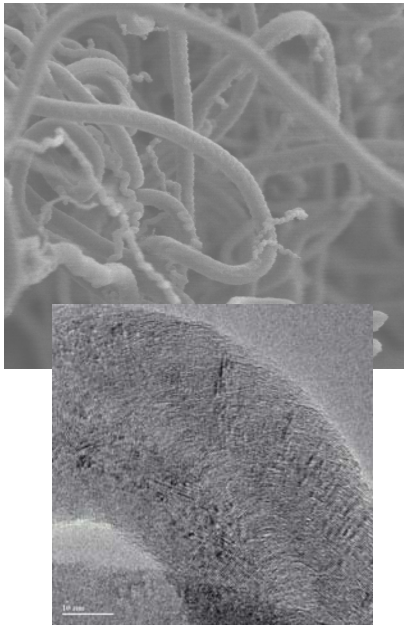
Pressure Range	Temperature	Pressure Resolution	Hydrogen Mass Resolution
0 – 10 Atm	0 °C	0.01 Atm	4.5×10^{-5} g H_2
0 – 10 Atm	100 °C	0.01 Atm	3.3×10^{-5} g H_2
0 – 10 Atm	400 °C	0.01 Atm	1.8×10^{-5} g H_2
10 – 65 Atm	0 °C	0.065 Atm	2.7×10^{-4} g H_2
10 – 65 Atm	100 °C	0.065 Atm	1.9×10^{-4} g H_2
10 – 65 Atm	400 °C	0.065 Atm	1.0×10^{-4} g H_2
65 – 200 Atm	0 °C	0.2 Atm	8.9×10^{-4} g H_2
65 – 200 Atm	100 °C	0.2 Atm	6.5×10^{-4} g H_2
65 – 200 Atm	400 °C	0.2 Atm	3.6×10^{-4} g H_2

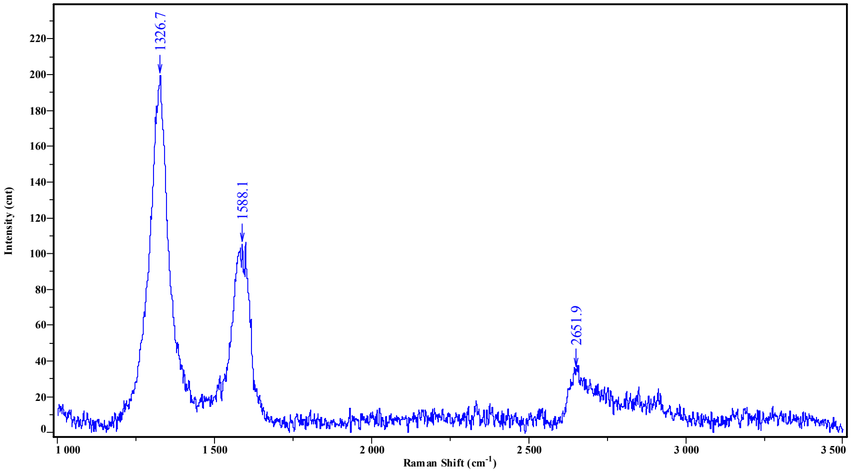
H_2 Storage ACCOMPLISHMENTS (CANDIDATE STORAGE MATERIALS)

Material Type	Examples	Advantages	Difficulties	Solution Approach
Nanostructural Materials	•Carbon Nanotubes •Amorphous Carbon •Carbon Nanofibers •Metal Organic Frameworks •Nanorods	•Reasonable Adsorption kinetics •Desorption is easily thermally reversible	•Adsorption process requires cryogenic temperatures •Samples can be inconsistent •Lower percent mass Hydrogen storage ~(.5% - 5%)	•Application of Hydrogen Dissociation Catalysts to Increase Adsorption Temperatures •Modify production techniques to increase surface area and quality
Magnesium and Magnesium Alloy Hydrides	(percent mass) •Mg-(10)Al •Mg- (25)Ni	•Higher percent mass Hydrogen storage ~(2.5%-7.5%) •Can easily be mass produced •Can have practical absorption and desorption kinetics •Stable if dry	•Hydride formation \ decomposition typically involves high temperatures (~400 °C) •Can sometimes require high pressures	•Substitution of new alloy metals •Introduction of catalytic compounds
Group III Hydride Complexes	•Li [AlH_4] •Na [AlH_4] •K [BH_4] •Na [BH_4]	•Very High Storage Capacity •Compounds range from ~7.5% to ~18.5% Hydrogen by mass •Stable if dry	•Direct hydride formation can be difficult •Covalent hydride gasses may form (e.g. B_2H_6) •Decomposition typically occurs at high temperatures	•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/La_2O_3 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 all the bands corresponding to Carbon nanostructures

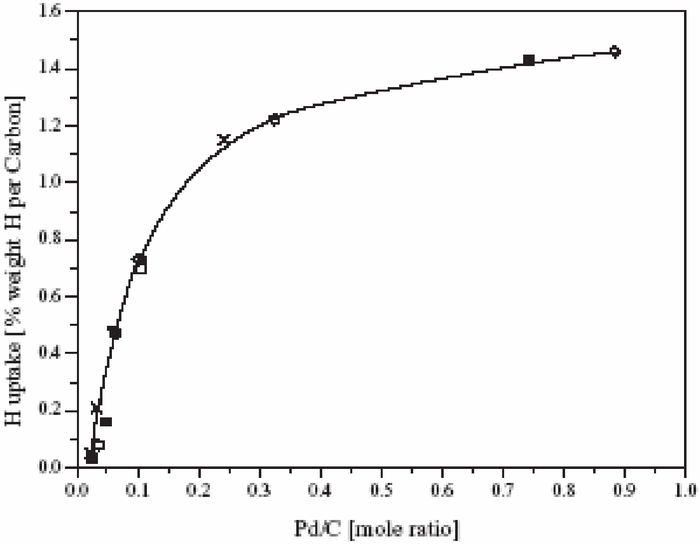
D band at 1326 cm^{-1}
G band at 1588.1 cm^{-1}
2D band at 2651.9 cm^{-1}

ACCOMPLISHMENTS

Pd/Carbon Nanofibers uptake system

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

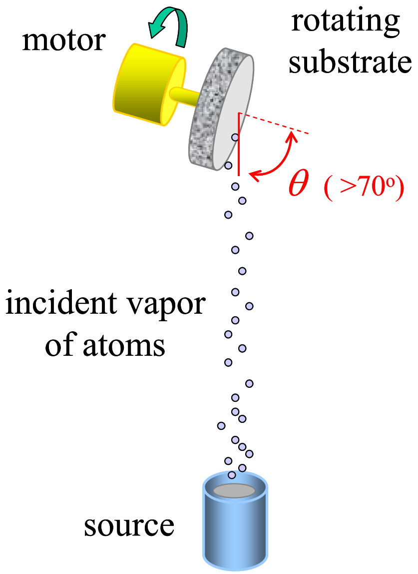
- There was found a direct correlation between the amount of adsorbed hydrogen and the Pd/C ratio. Basically, an increase in the amount of metallic Pd corresponds to a higher hydrogen adsorption value on the carbon nanofibers.



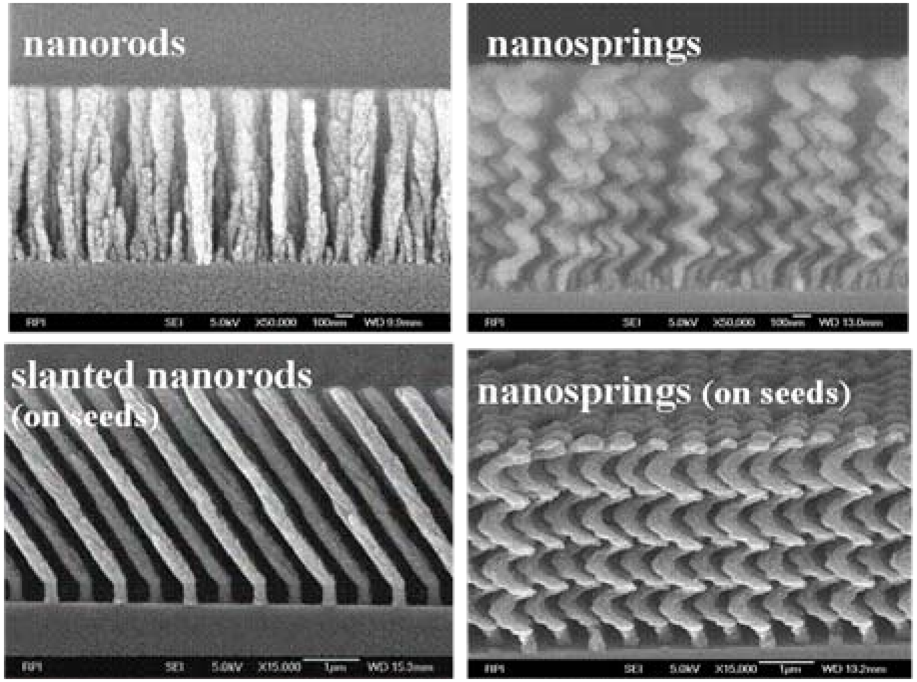
- These results can be explained by
  - **the catalytic properties of the Pd particles that dissociate H_2 into atomic H.**
  - **the possible charge transfer between Pd and C, given the work function difference between palladium (5.1-5.6 eV) and carbon nanofibers (4.9-5.05 eV). The relationship between 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):



Oblique angle deposition: *Kundt, Ann. Phys. Chem. Lpz. 27, 59 (1886).* *Oblique angle deposition with rotation:* *Young and Kowal, Nature 183, 104 (1959); Robbie, Brett, and Lakhtakia, Nature 384**,** 616 (1996)*

Reviews:

- *Karabacak and Lu, in Handbook of Theoretical and Computational Nanotechnology, edited by M. Rieth and W. Schommers (American Scientific Publishers, 2005), chap. 69.*
- *Lakhtakia and Messier, Sculptured Thin Films: Nanoengineered Morphology and Optics, SPIE Press, Bellingham, Washington (2005)*

H_2 Storage

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

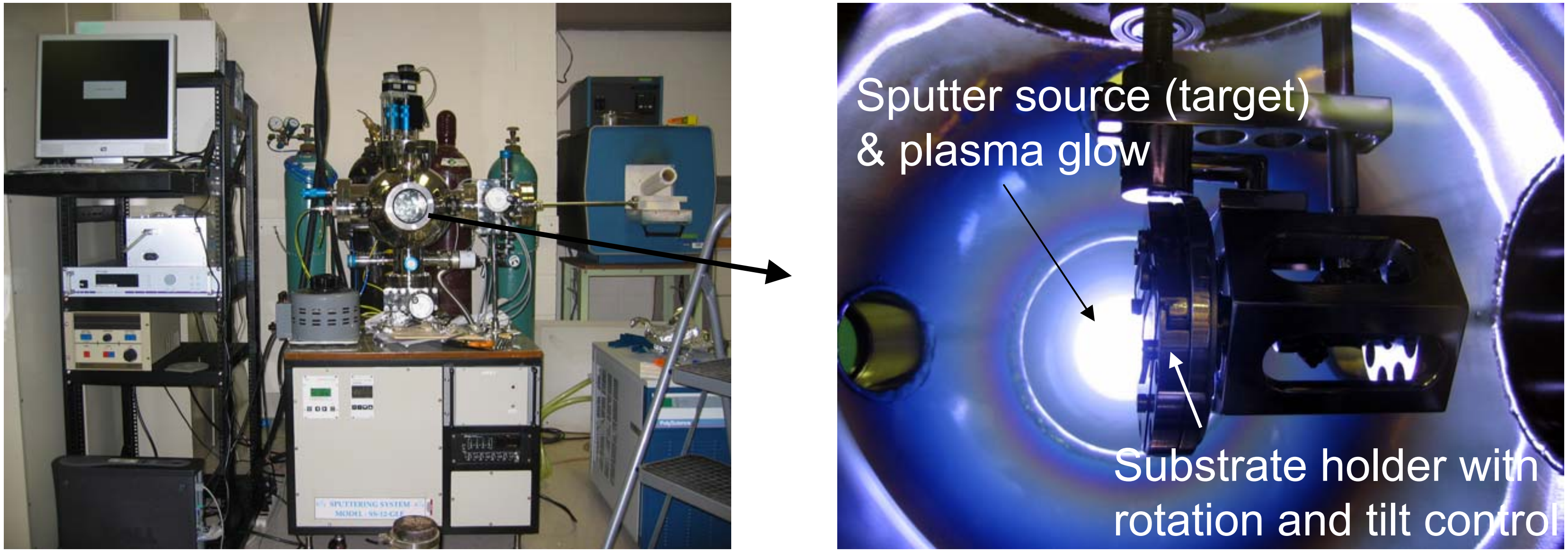
Obliquely deposited nanorods and nanosprings of metal hydrides are expected to provide superior hydrogen storage properties because of:

- ***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.

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

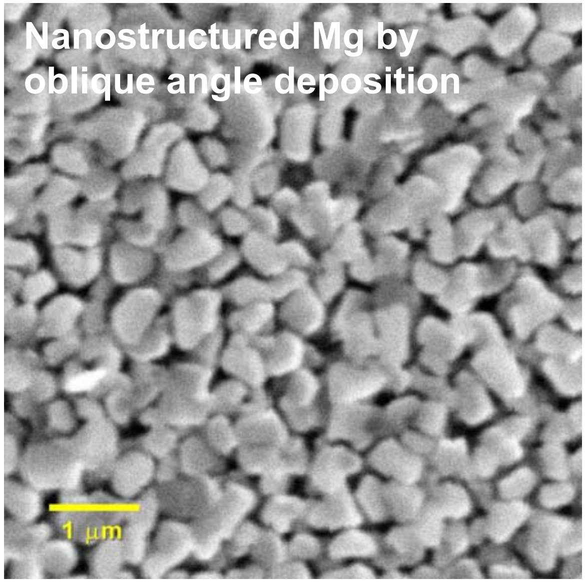
H_2 Storage

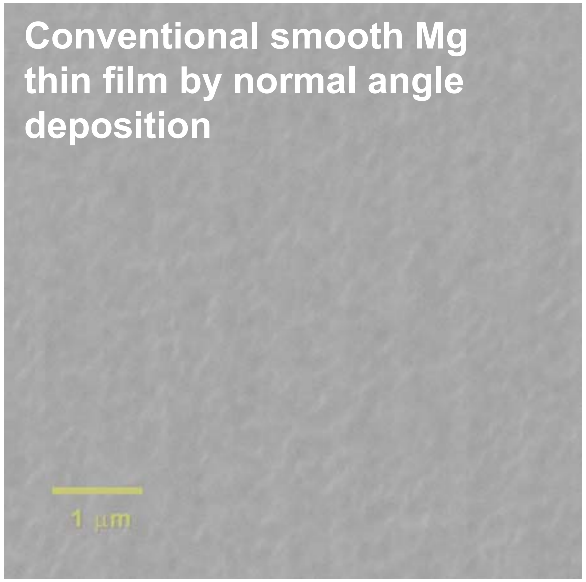
ACCOMPLISHMENTS

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

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

Top view SEM pictures of nanostructural Mg and conventional Mg thin films (scale bar is 1μm)





Deposition Parameters	**Nanostructured Mg** (ID030407_1)	**Conventional Mg thin film** (ID030607_1)
Deposition Angle:	85 °	0 °
Substrate Rotation speed:	5 RPM	1 RPM
DC Power:	100 Watts	100 Watts
Deposition Time:	60 mins	37 mins
Base Pressure:	2.4*10-7 mbar	3.1*10-7 mbar
Ar Pressure:	3.0*10-3 mbar	3.0*10-3 mbar
MFC:	2.9 ccm	3.1 ccm
Film Thickness:	~1 μm	~1 μm

➢ ***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)***

H_2 Storage

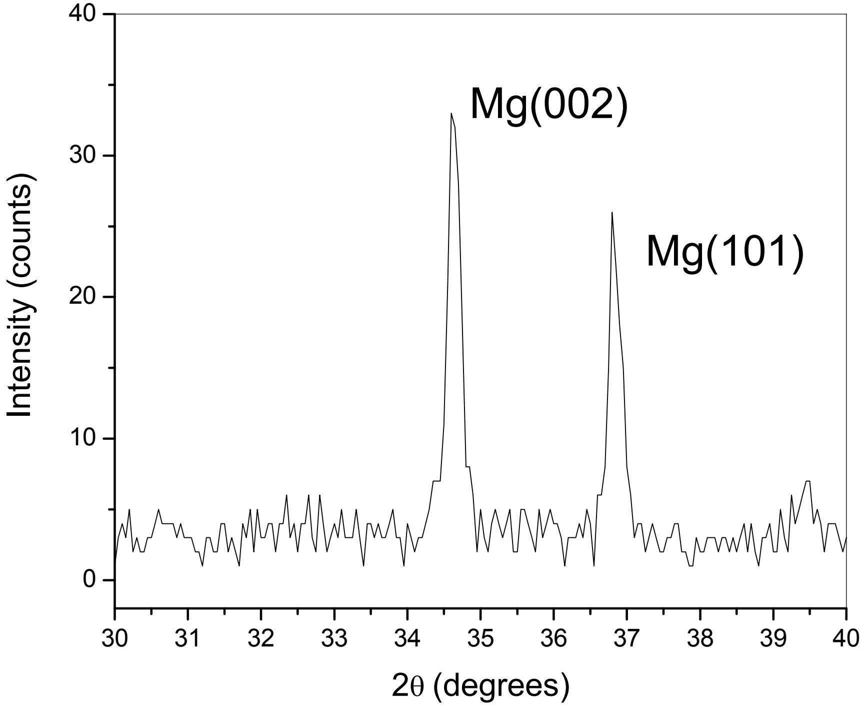
ACCOMPLISHMENTS

- ***Crystal Orientation (Texture):***

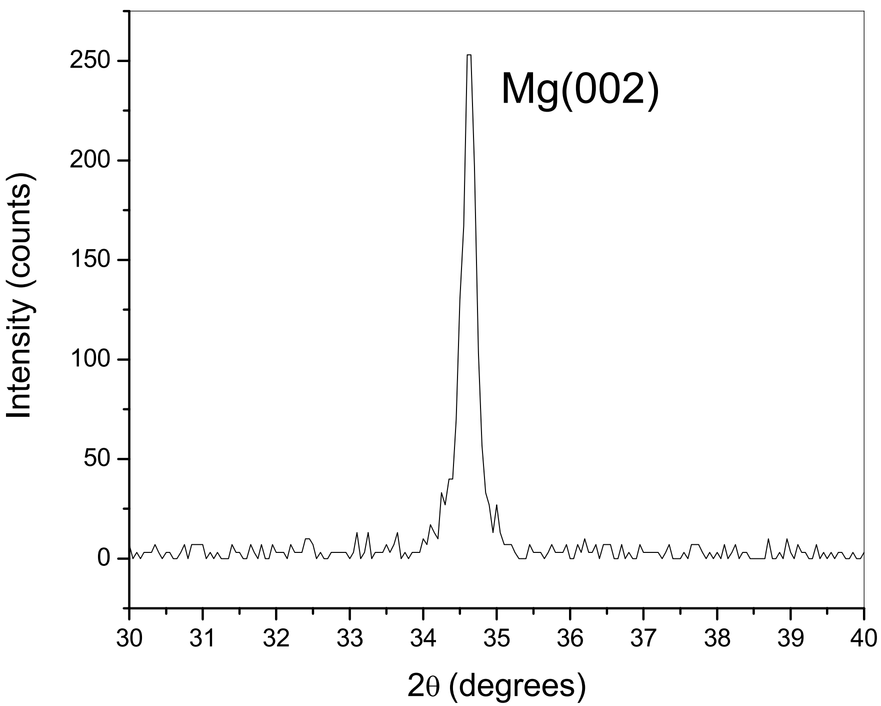
- ***Development of (101) texture in nanostructured Mg films while conventional Mg films is highly (002) oriented: (101) oriented nanostructures is likely to have different H2 absorption/desorption kinetics compared to (002) oriented thin films.***

- ***No oxidation peaks have been observed***

Nanostructured Mg by oblique angle deposition



Conventional smooth Mg thin film by normal angle deposition



Summary

- A dye sensitized solar cell was designed and fabricated; (**H_2 production**)
- Plasma surface was employed for surface modification of nanocrystalline TiO2 used as an electrode in Photoelectrochemical cell; (**H_2 production)**
- A novel oblique angle sputter deposition technique in order to grow nanostructured Mg films for hydrogen storage applications was utilized;(**H_2 storage**)
- Initial results show that Mg nanostructures have high surface to volume ratios apparent with superior effective surface area values;(**H_2 storage**)
- Crystal orientation of Mg nanostructures are also quite different than the conventional thin films of Mg; (**H_2 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**)