Solar Powered High Temperature Photochemical Water Splitting

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Research Goals and Objectives

- Produce hydrogen using resources available in Florida without GHG emissions
- Utilize both solar heat & photonic energy to increase hydrogen production efficiency
- Develop a new thermochemical water splitting cycle that is optimum for solar interface
- Synthesize highly efficient & selective photocatalysts

Relevance to Current State-of-the-Art

- Solar thermochemical splitting of water for hydrogen production is a carbon free process that is presently of great interest to the scientific community
- Thermochemical water splitting cycles have been shown to be more efficient method for hydrogen production from water than those that utilize water electrolysis, high temperature direct splitting or other techniques
- FSEC is developing an innovative cycle that is one of only few true solar-based thermochemical water-splitting cycle in the world

Relevance to NASA

- Local hydrogen production for NASA-KSC using a renewable carbon-free energy source
- Technology developed can be used on the Moon & in space

Budget, Schedule and Deliverables

- **Budget: $185,000**

- **Schedule:**
  1st quarter: Experimental setup & feasibility tests
  2nd quarter: UV light photolytic H_2 production
  3rd quarter: Solar H_2 production
  4th quarter: Photocatalyst screening

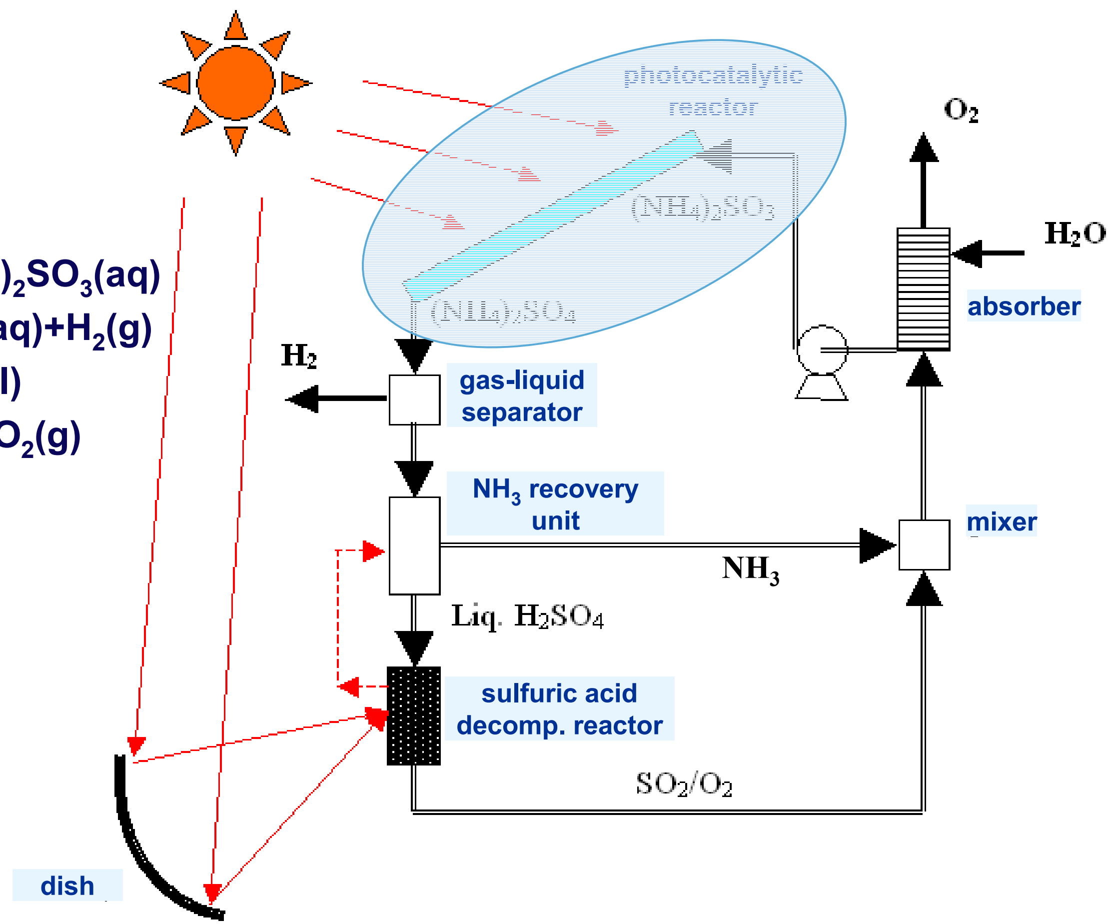
- **Deliverables:**
  1 - A solar thermochemical process for production of H_2 from H_2O
  2 – Preparation of nanosized photocatalyst particles & photoelectrodes
  3 – development of a method for the photocatalyst preparation
  4 - Process design & optimization

Anticipated Technology End Use

- Local hydrogen production for the NASA Kennedy Space Center
- Inexhaustible H_2 production for hydrogen economy
- Space exploration - H_2 production in space and on the Moon & Mars
- Technology developed can be employed for O_2 production
- Technology developed can potentially be used for O_2 production from lunar soil

A New S-A Thermochemical Water Splitting Cycle

$SO_2(g) + 2NH_3(g) + H_2O(l) \rightarrow (NH_4)_2SO_3(aq)$
$(NH_4)_2SO_3(aq) + H_2O \rightarrow (NH_4)_2SO_4(aq) + H_2(g)$
$(NH_4)_2SO_4(aq) \rightarrow 2NH_3(g) + H_2SO_4(l)$
$H_2SO_4(l) \rightarrow SO_2(g) + H_2O(g) + 1/2O_2(g)$



UV Photolytic H_2 Production

Advantages:

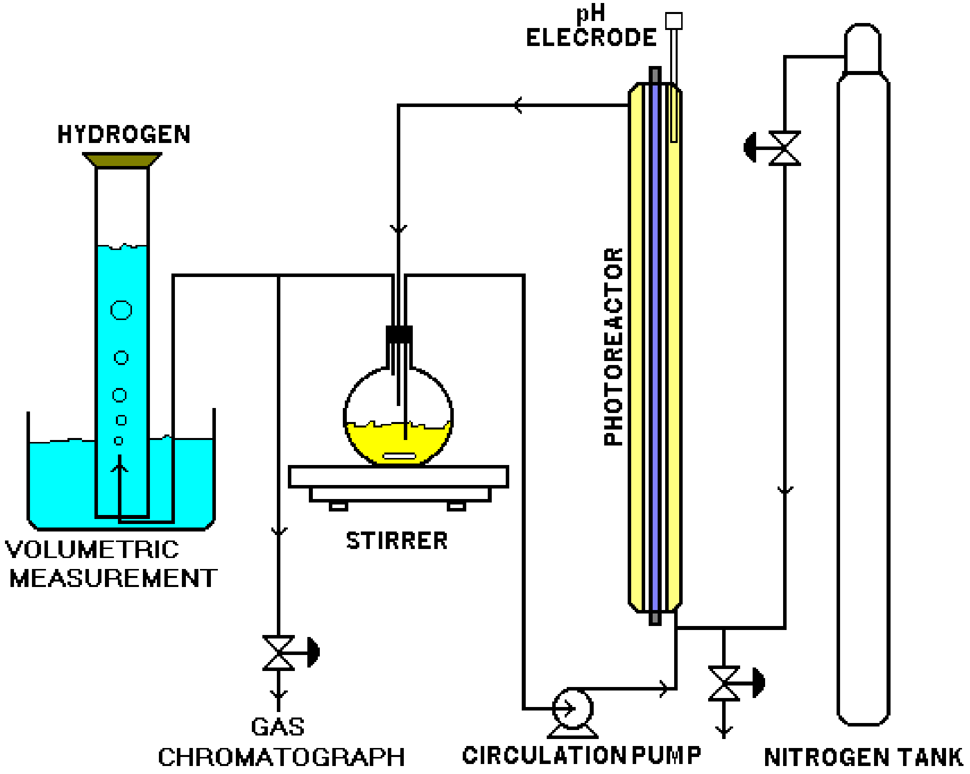
- No catalyst is needed
- Higher efficiency
- Low cost & less complicated
- Potentially applicable in space & on the Moon

Results:

- Optimized reaction conditions (temperature, pH, concentration)
- Investigated reaction mechanisms
- Calculated material balance
- Determined H_2 production rate & efficiency (>30% UV to H_2)

Reaction:

$(NH_4)_2SO_3 + H_2O +$ **UV light** $\rightarrow (NH_4)_2SO_4 + H_2$

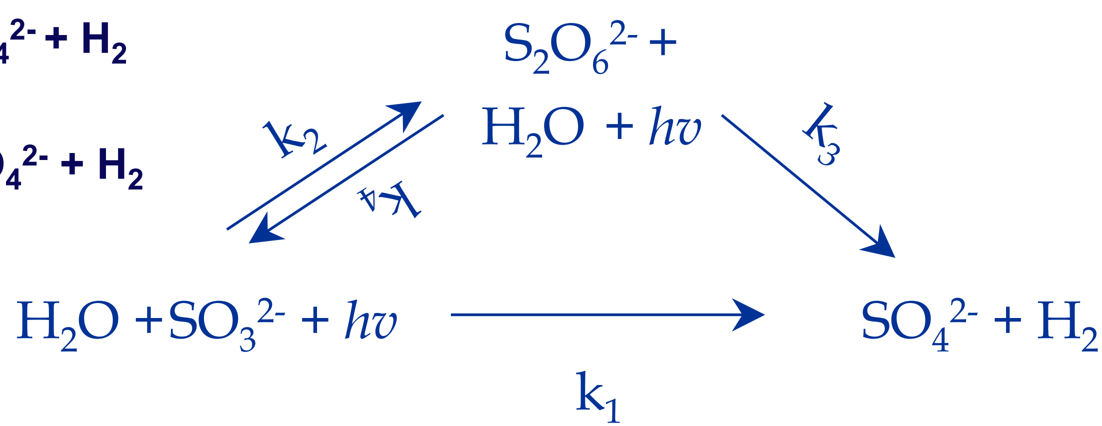


Results: UV Photolytic H_2 Production - Reaction Mechanism & Material Balance

(I) $H_2O + SO_3^{2-} + h\nu = SO_4^{2-} + H_2$

(II) $2SO_3^{2-} = S_2O_6^{2-}$

$S_2O_6^{2-} + H_2O + h\nu = SO_4^{2-} + H_2$



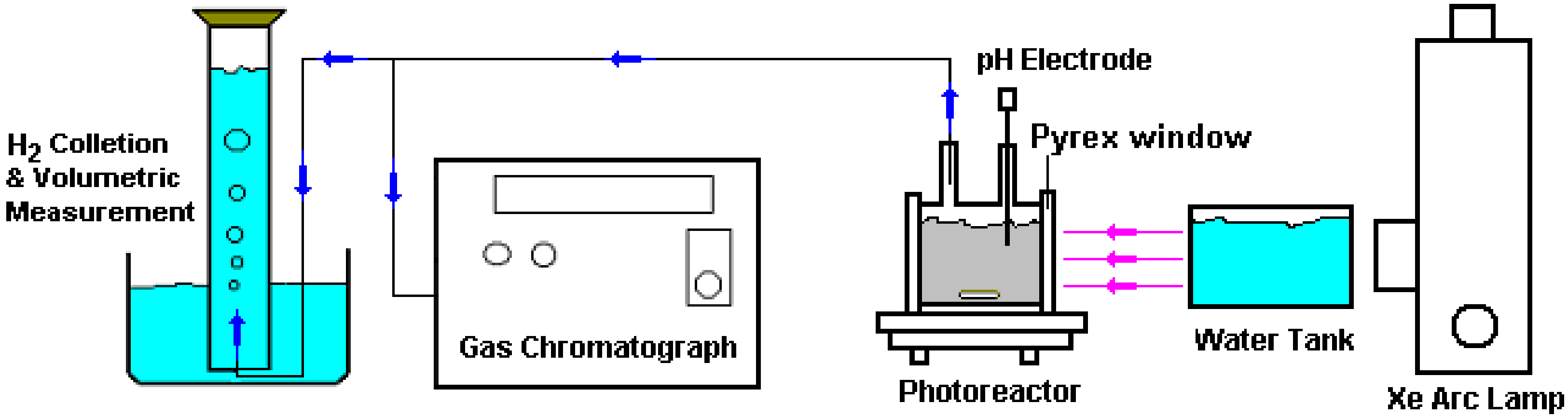
Average	Component	In (mol)	Out (mol)	Prod/Cons.(mol)	%Difference
Liquid Phase	SO_3^{2-}	0.040606	0.000000	0.040606	0.920415
	SO_4^{2-}	0.014432	0.054665	0.040232	
Gas Phase	H_2	Expected H_2 (mL)	Actual H_2 (mL)	Difference (mL)	% Diff
		986.9	909.0	77.9	7.9

Solar Photocatalytic H_2 Production

- **Reaction:**

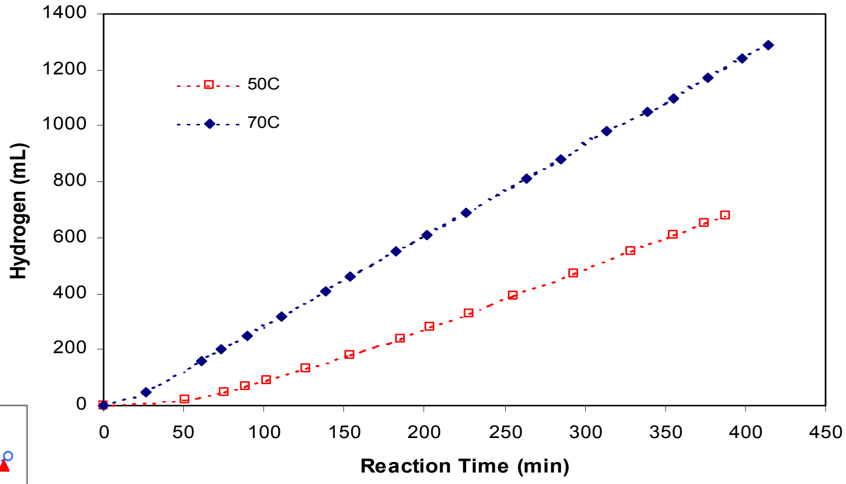
$(NH_4)_2SO_3 + H_2O +$ **sunlight +catalyst** $\rightarrow (NH_4)_2SO_4 + H_2$

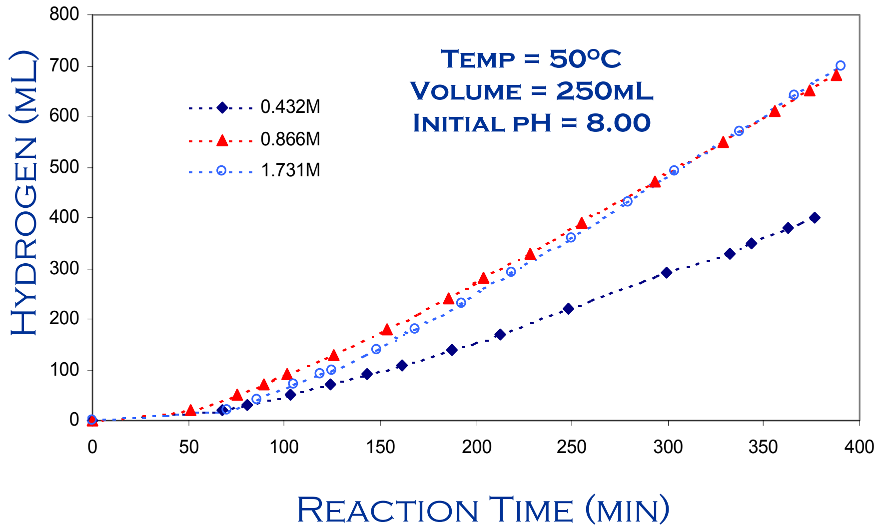
- **Experimental Setup & Photoreactor**
- **Results:** Concentration, Temperature, Platinum Loading, Catalyst Lifespan, Catalyst Screening, Kinetics, Process Efficiency



Results - Solar H_2 Production (1)

Temperature has a significant affect on H_2 production rate. The optimal temperature is in the range of 50 to 70°C. Solar heat can increase reaction rate

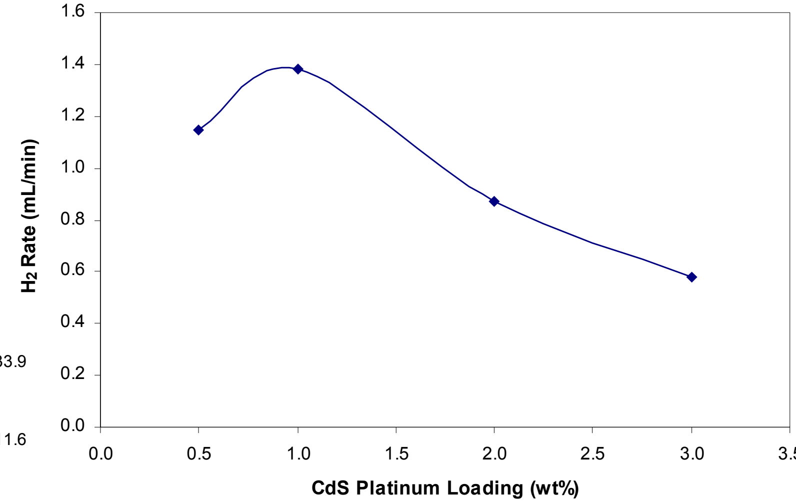


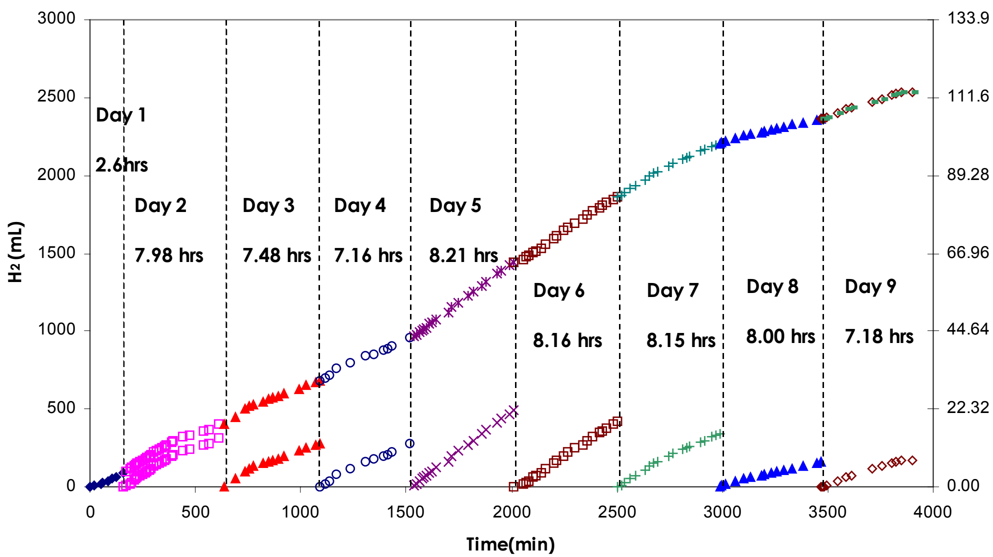


Concentration of Sulfite solution affects H_2 evolution rate. Optimal concentration is in the range of 0.8 to 1.0 M

Results - Solar H_2 Production (2)

Optimal Pt loading is 0.5 to 1.0% wt of CdS catalyst weight which is 0.01 % wt of reaction solution





Lifespan of Catalyst is expected to exceed 100 hours with SO_3^{2-} totally converted to SO_4^{2-}

Results - Solar H_2 Production (3)

Photocatalyst Screening

- ❑ Platinum doped CdS photocatalyst is highly efficient in converting $SO3^{2-}$ to $SO4^{2-}$
- ❑ CdS activity depends strongly upon the Pt dopant size
- ❑ Four techniques were used to prepare the catalysts including synthesizing nanosized Pt particles from chloroplatinic acid solution
- ❑ Superior techniques involved: 1) sodium borohydride reduction & 2) polymer protected process for Pt nanoparticle preparation

Process efficiency

- ❑ For the H_2 production, the light *(λ < 450 nm)* to hydrogen chemical energy conversion efficiency was about **12%**. Efficiency of **25-30%** is achievable
- ❑ Solar thermal energy can be utilized to elevate temperatures & increase the reaction rates

Future Plans

- Identify more effective photocatalysts capable of absorbing light with λ in the visible region
- Develop novel photoreactors to increase the photoefficiency of solar light harvesting
- Perform closed loop S-NH_3 tests
- Find new techniques for preparing nanosize photocatalysts
- Explore the application of the S-NH_3 cycle for O_2 production
- Seek additional U.S. DOE & other Agency support – DOE has already committed $500k as FY’06 funding

Patents and Publications

Patents:

One provisional patent has been filed and one is under preparation

Publications:

- Cunping Huang, Olawale Adebiyi, Nazim Muradov, Ali T-Raissi, "UV Photolysis of Ammonium Sulfite Aqueous Solution for the Production of Hydrogen," *16th World Hydrogen Energy Conference*, Lyon, France, June 13-16, 2006
- Ali T-Raissi, Cunping Huang, Nazim Muradov, Olawale Adebiyi, "Production of Hydrogen via a Sulfur-Ammonia Solar Thermochemical Water Splitting Cycle," *16th World Hydrogen Energy Conference*, Lyon, France, June 13-16, 2006
- Ali T-Raissi, Cunping Huang, Nazim Muradov, Olawale Adebiyi, "Production of Hydrogen by Solar Water Splitting via Hybrid Sulfur-Ammonia Cycle," *NHA Annual Meeting* 2006, Long Beach, CA, March 12-16, 2006
- Muradov, N., T-Raissi, A., Huang, C., Adebiyi, O., Taylor, R. and Davenport, R., "Solar hybrid water-splitting cycles with photon component," *2nd European Hydrogen Energy Conference*, Zaragoza, Spain, November 22-25, 2005
- Ali T-Raissi, Nazim Muradov, Cunping Huang, "Solar Hydrogen via High-Temperature Water-Splitting Cycle with Quantum Boost," *International Solar Energy Conference & Journal of Solar Engineering*, Orlando, USA, August 6-12, 2005

Thank You

Questions?