

# Solar Energy Utilization

Using (1)  $\text{TiO}_2$  nanotubes (T\_NT), (2) T\_NT /CdSe, and (3)  $\text{TiO}_2$ /CdS/Pt  
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Presenter | Vaidyanathan (Ravi) Subramanian

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(This presentation does not contain any proprietary, confidential, or otherwise restricted information)

# Overview

## Timeline

- 1/1/2011-12/31/2011
- 1/1/2012- 9/30/2012  
(no cost extension)

## Budget\*

- Total funding
  - 258,235.00 (UNR)
  - 53,402.00 (cost share)

## Personnel

- 1 post-doc
- 2 graduate students
- 4 undergraduates

## Barriers

- Develop cost effective approach to growing TiO<sub>2</sub> nanotubes with added architectural flexibility
- Improve efficacy of coating visible light harvesters
- Determine effects of pollutants in hydrogen generation using traditional photocatalysts

## Partners

- Desert Research Institute
- University of Nevada, Reno



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# Milestones



Barriers	Progress	% activity completed
(Barrier 1) Cost effective approach	<ul style="list-style-type: none"><li>• Method development</li><li>• Testing the nanotubes physical features</li><li>• Testing the photocatalytic activity</li></ul>	100 % (manuscript published)
(Barrier 2) Improve coating process	<ul style="list-style-type: none"><li>• Solvothermal coating</li><li>• Examining coat density</li><li>• Develop mechanism</li><li>• Test activity</li></ul>	80 % (manuscript submitted)
(Barrier 3) H <sub>2</sub> generation + waste treatment	<ul style="list-style-type: none"><li>• Develop assembly</li><li>• Gather preliminary data</li><li>• How does pollutant influence H<sub>2</sub> yield</li><li>• Mechanistic studies</li></ul>	60 % (Research continuing)



# *Barrier 1 – Cost*

## *(Method for synthesis)*

- Objective - evaluate if the nanotubes can be grown on flexible substrates with minimal usage of electrolyte
  - Goal – To study the anodization conditions with the intent to minimize Ti and electrolyte usage (reduce cost) without compromising on TiO<sub>2</sub> nanotube quality and properties

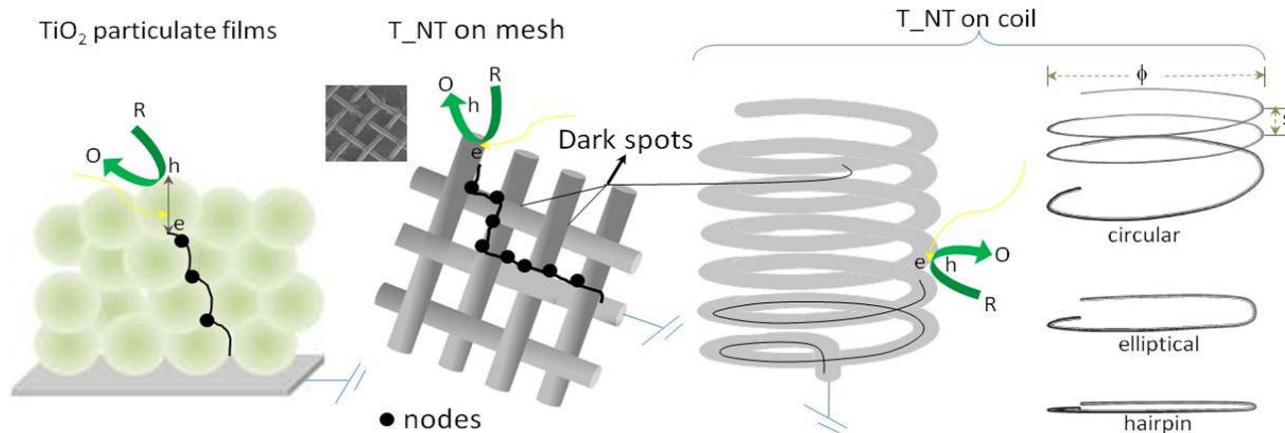
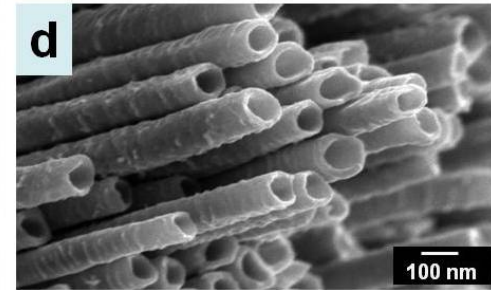
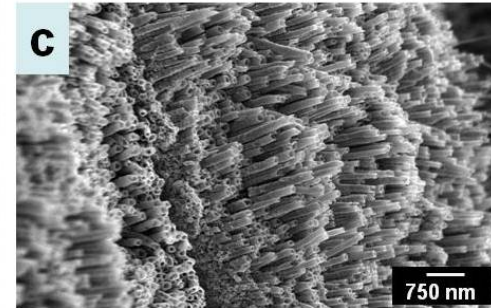
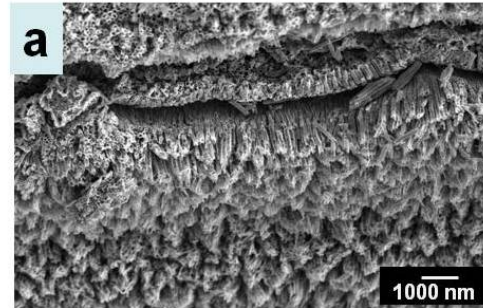
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<b>Performance measure</b>	<b>Method I</b>	<b>Method II</b>	<b>Outcome</b>
Electrolyte volume	~300 ml	~25 ml	TiO <sub>2</sub> nanotubes
Geometry independence	foil	coil	TiO <sub>2</sub> nanotubes

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# Barrier 1 – Cost (SEM images)

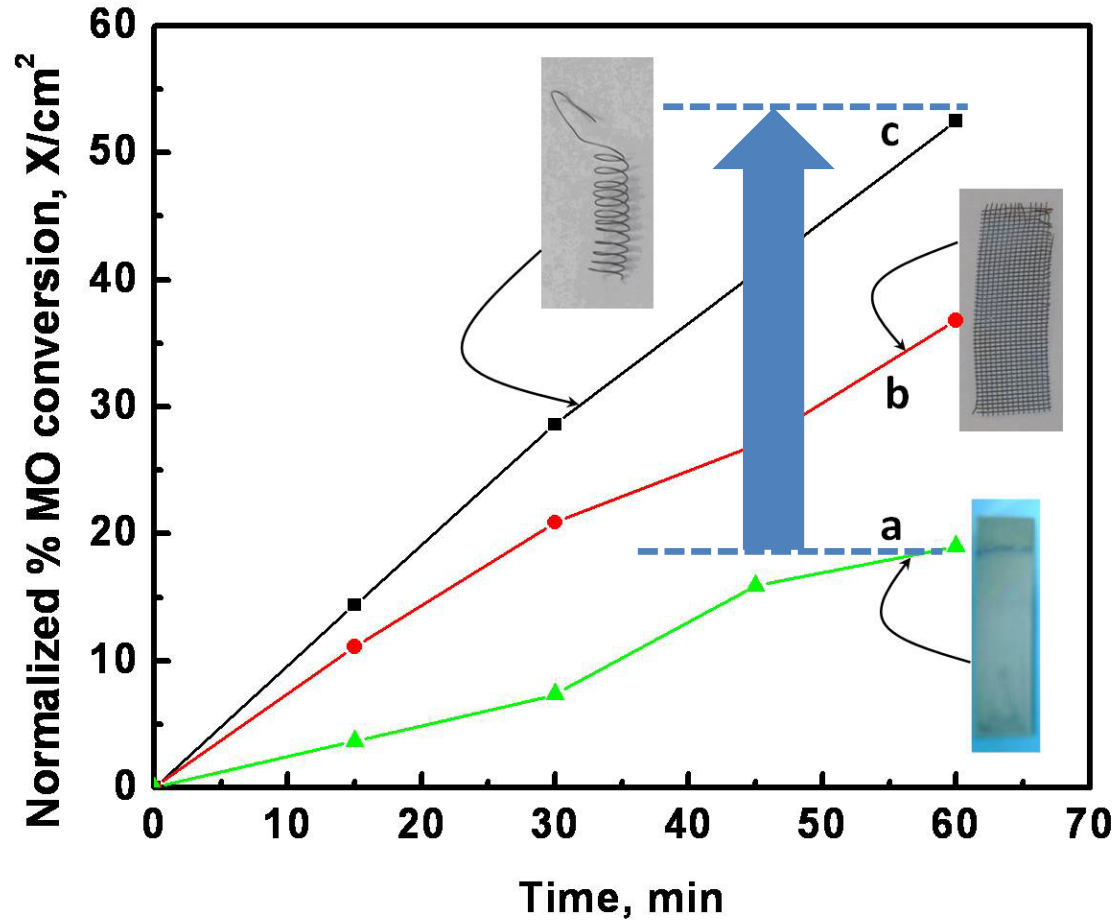
- TiO<sub>2</sub> nanotubes (T\_NT) formed on coil using 25 ml electrolyte instead of 300 ml electrolyte
- Progressive images indicate clearly the formation of nanotubes
- Similar nanotubes have been demonstrated on foil, mesh, and wires



# Barrier 1 – Cost

## (Photoactivity: Liquid)

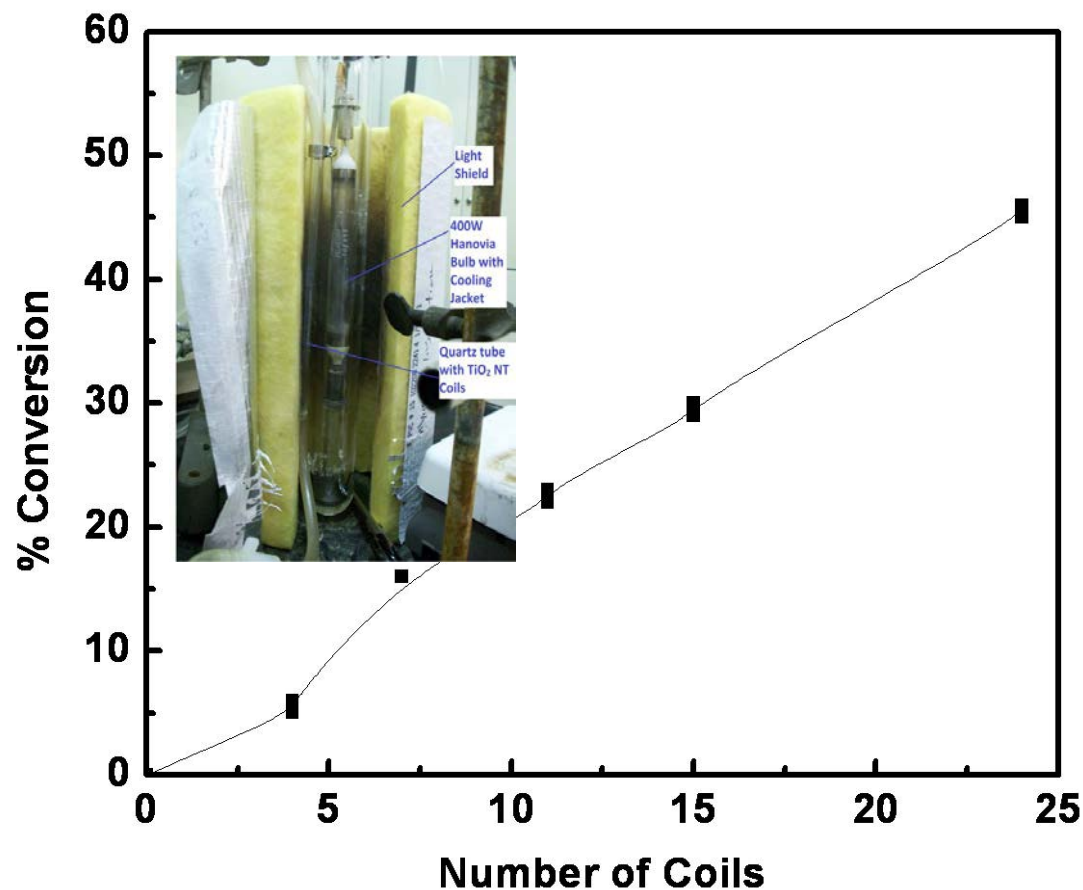
- Photoactivity of the T\_NT on coil is compared with nanotubes on other substrates prepared using method I
- Test compound: methyl orange
- x 2.5 times increase in photodegradation is observed with T\_NT on coils.  
[Normalized to geometrical surface area of illumination]



# Barrier 1 – Cost

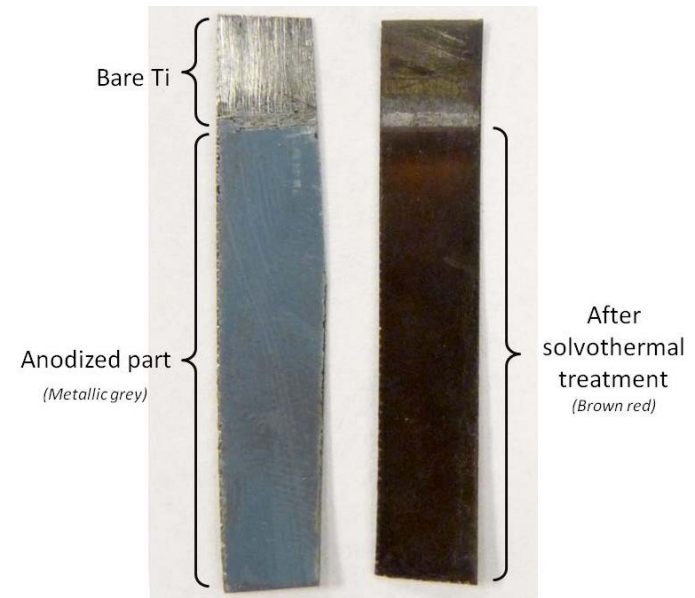
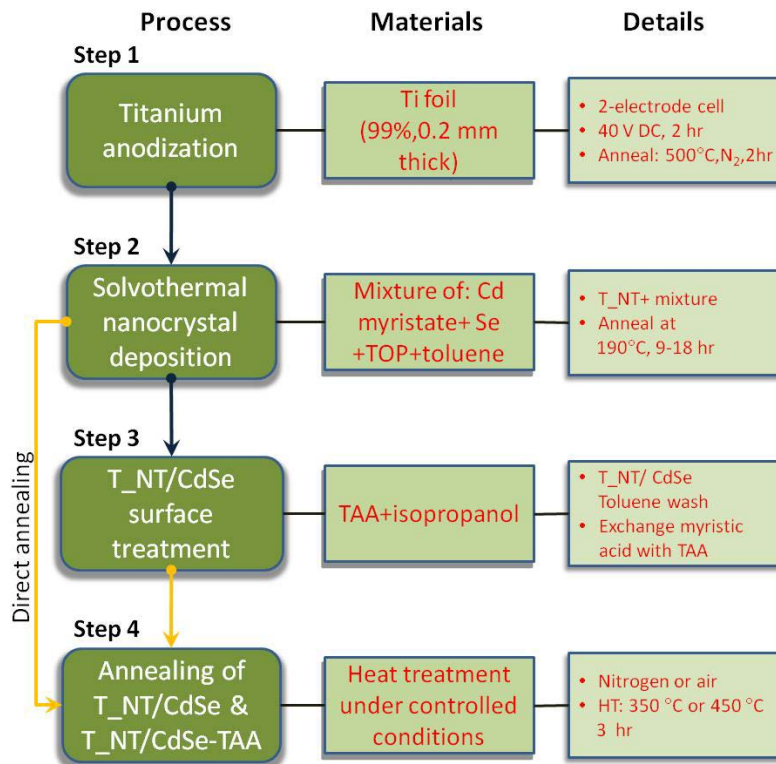
## (Photoactivity: Gas phase)

- The applicability of T<sub>NT</sub> as a photocatalyst on coil for gas phase catalysis has also been studied
- Test compound: 2,3-butanedione
- Up to 40% conversion of the gas phase pollutant is demonstrated (un-optimized) in a single pass gas phase photocatalytic reactor



# Barrier 2 – Coating (Solvothermal approach)

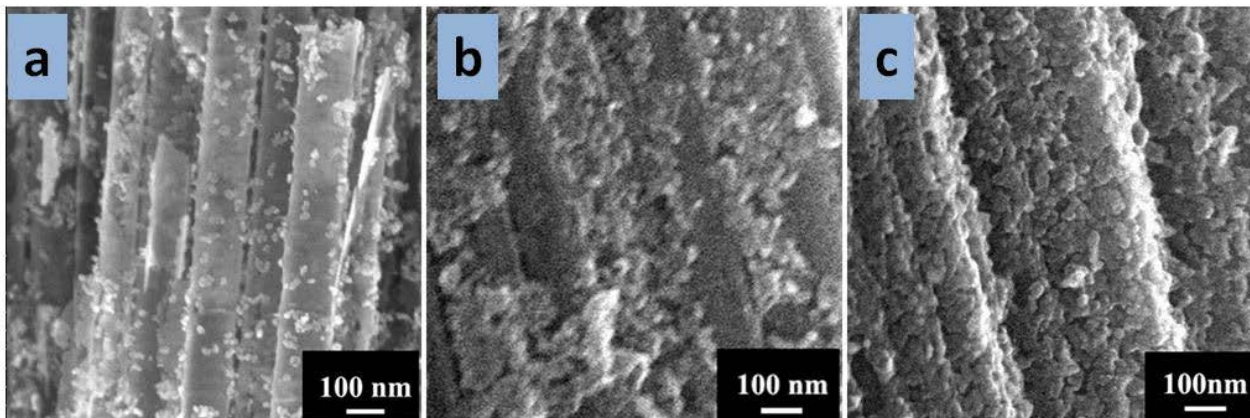
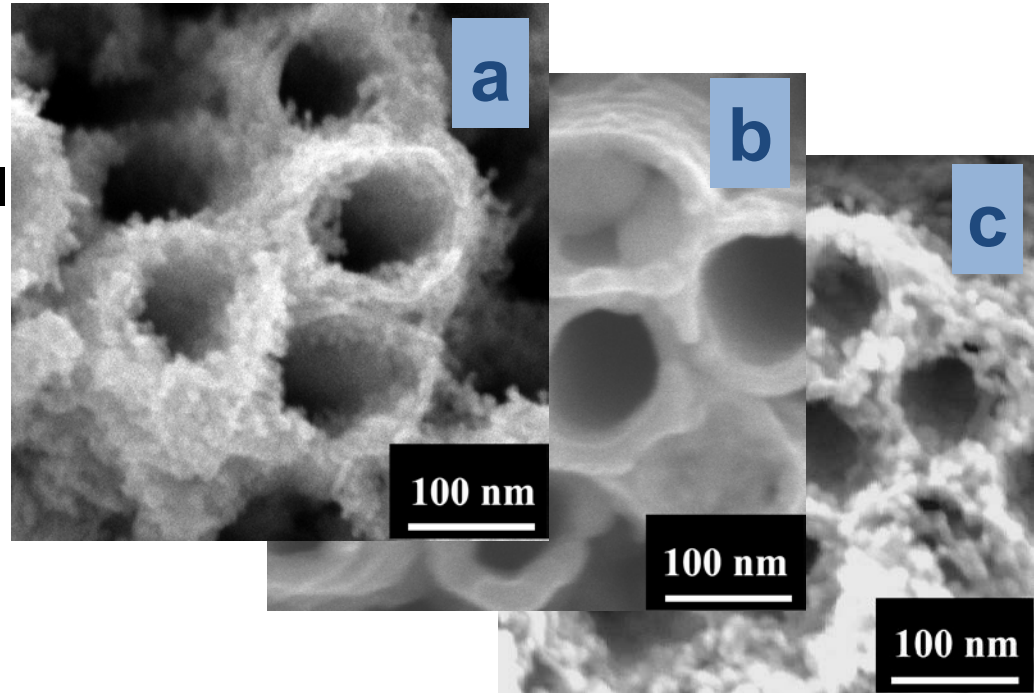
- Objective – To develop an efficient coating strategy
  - Goal – To determine if a solvothermal approach with a ligand treatment can form dense CdS deposits on the T\_NT walls
  - A review of literature followed by compilation of an article has been carried out as the basis for this research





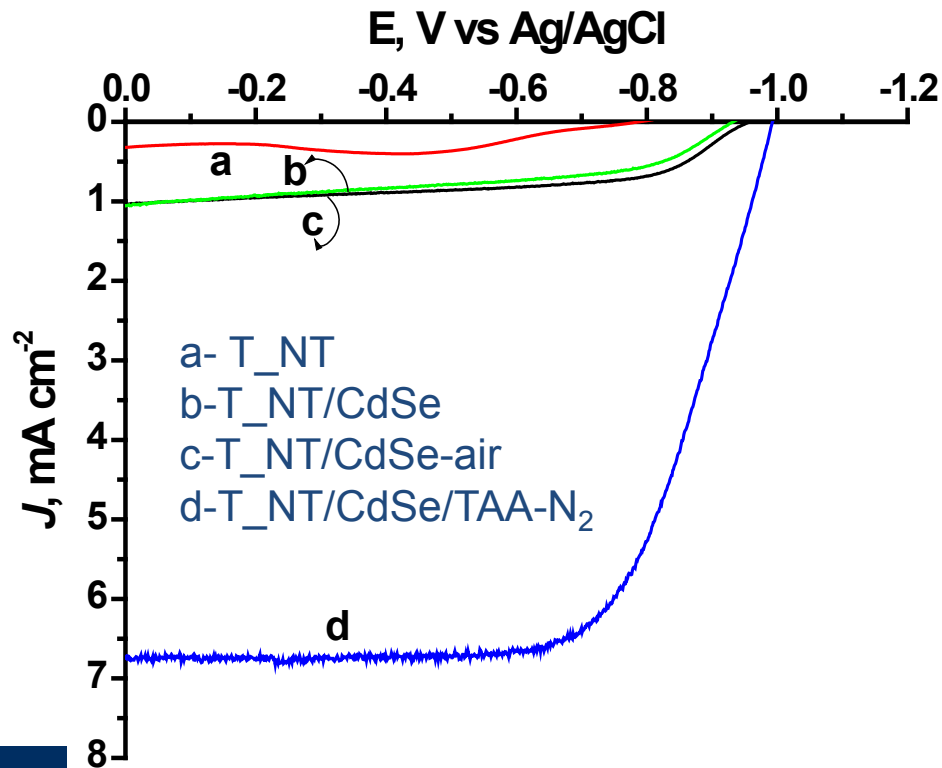
# Barrier 2 – Coating (SEM images)

- The SEM images indicate a uniform coating on the T\_NT walls under solvothermal conditions
- A ligand treatment assists with maintaining dense coating and particle size
  - a- T\_NT/CdSe
  - b-T\_NT/CdSe-no exchange
  - c- T\_NT/CdSe-ligand exchange

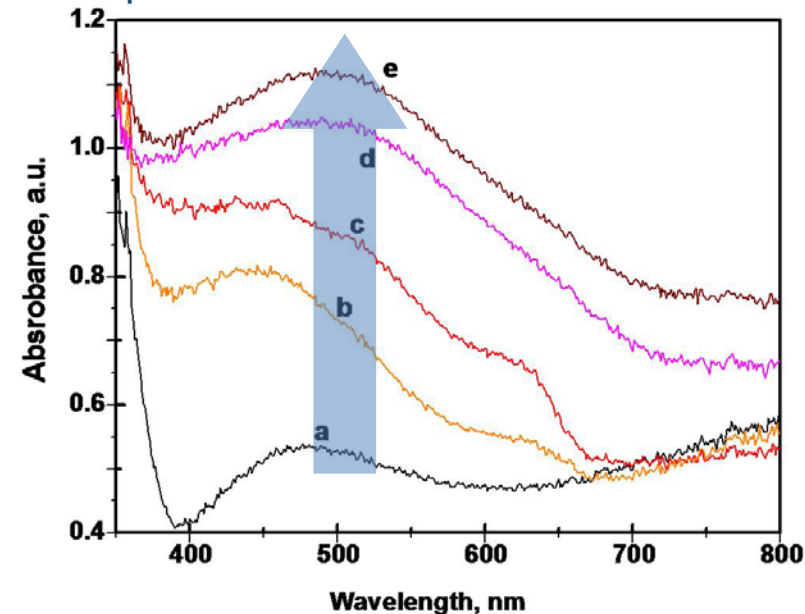


# Barrier 2 – Coating (optical & electronic activity)

- The CdSe deposits via a solvothermal approach followed by a ligand exchange gives maximum photocurrent

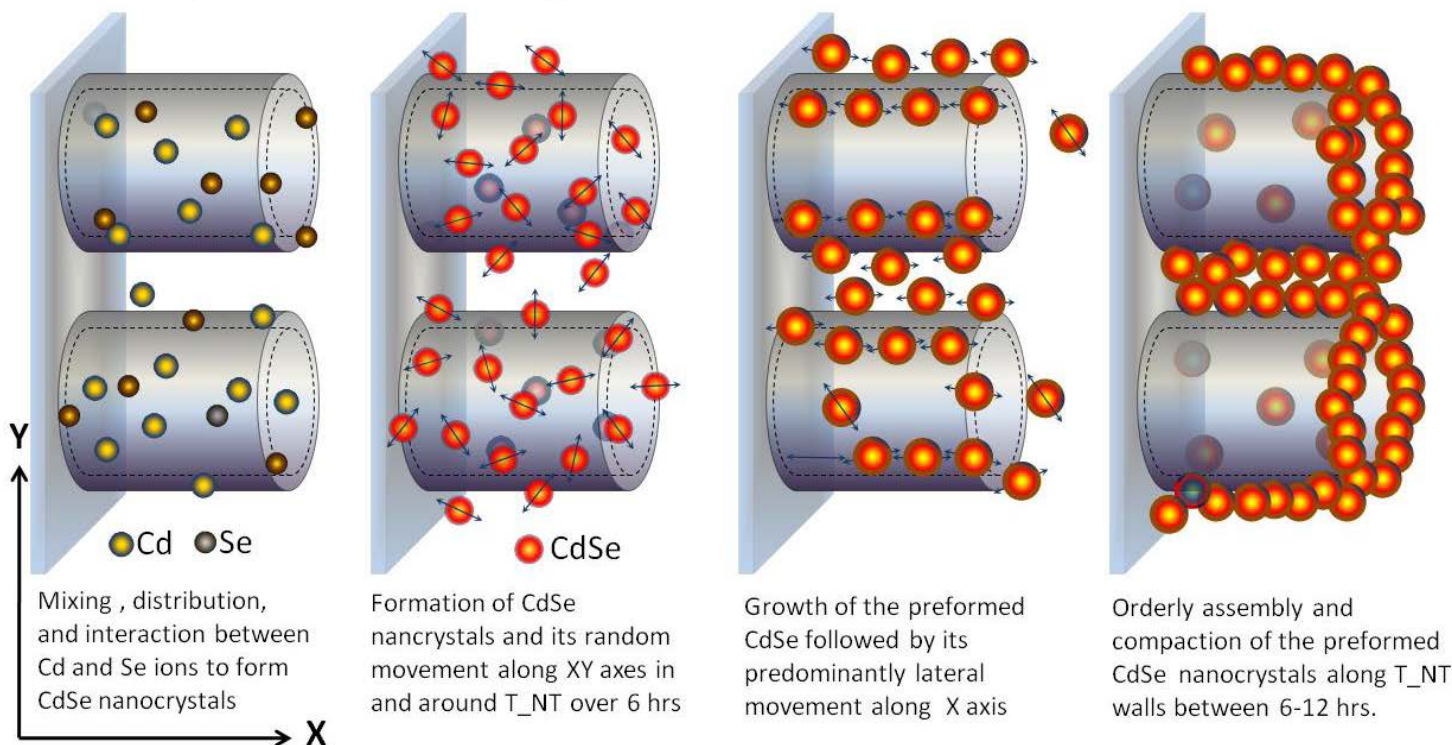


More exposure to solvothermal conditions leads to increase in CdSe deposits



# Barrier 2 – Coating (Coating mechanism)

- A 4-step process is believed to take place during CdSe deposition on T\_NT when the solvothermal treatment is followed by annealing under nitrogen after ligand treatment



# Barrier 3 – Fuel+waste (Photocatalyst synthesis)

- Objective – To examine strategies to improve photocatalytic hydrogen generation and waste treatment - simultaneously
  - Goal – To determine if a photocatalyst can produce hydrogen and photodegrade a liquid phase pollutant

## Step 1

Titanium dioxide  
(IH-TiO<sub>2</sub>)

Hydrothermal approach

## Step 2

Metal nanoparticle

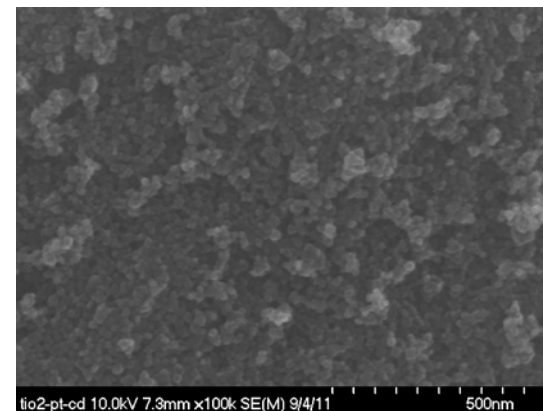
Au, Pt, and Ag

## Step 3

CdS nanoparticle

Cd and S salts

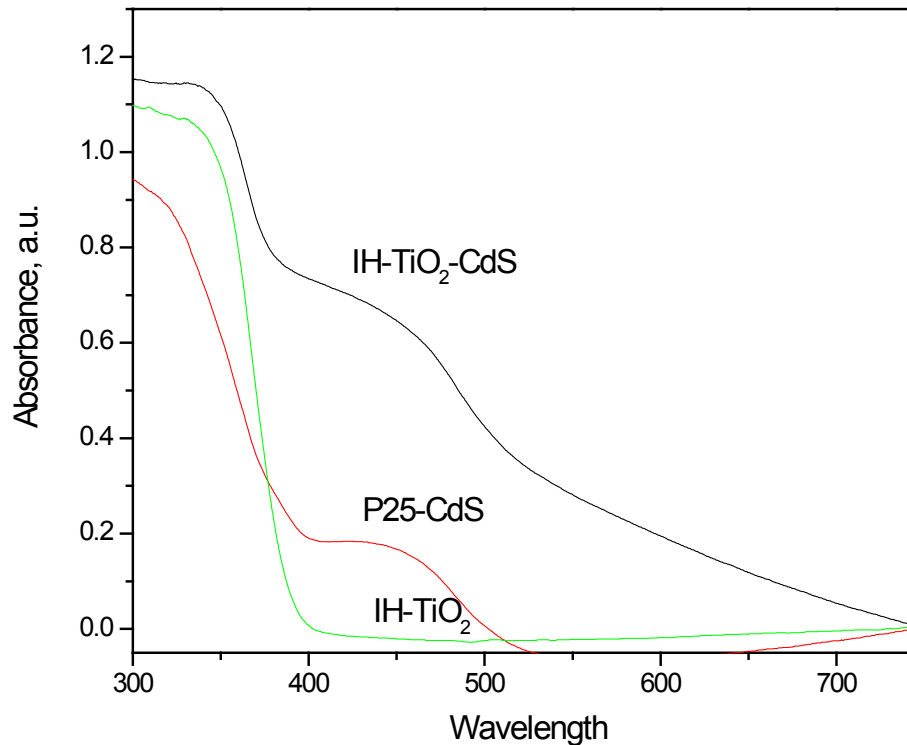
Step 4



Sample	Surface Area (m <sup>2</sup> /g)
IH-TiO <sub>2</sub>	~130
P25	~53

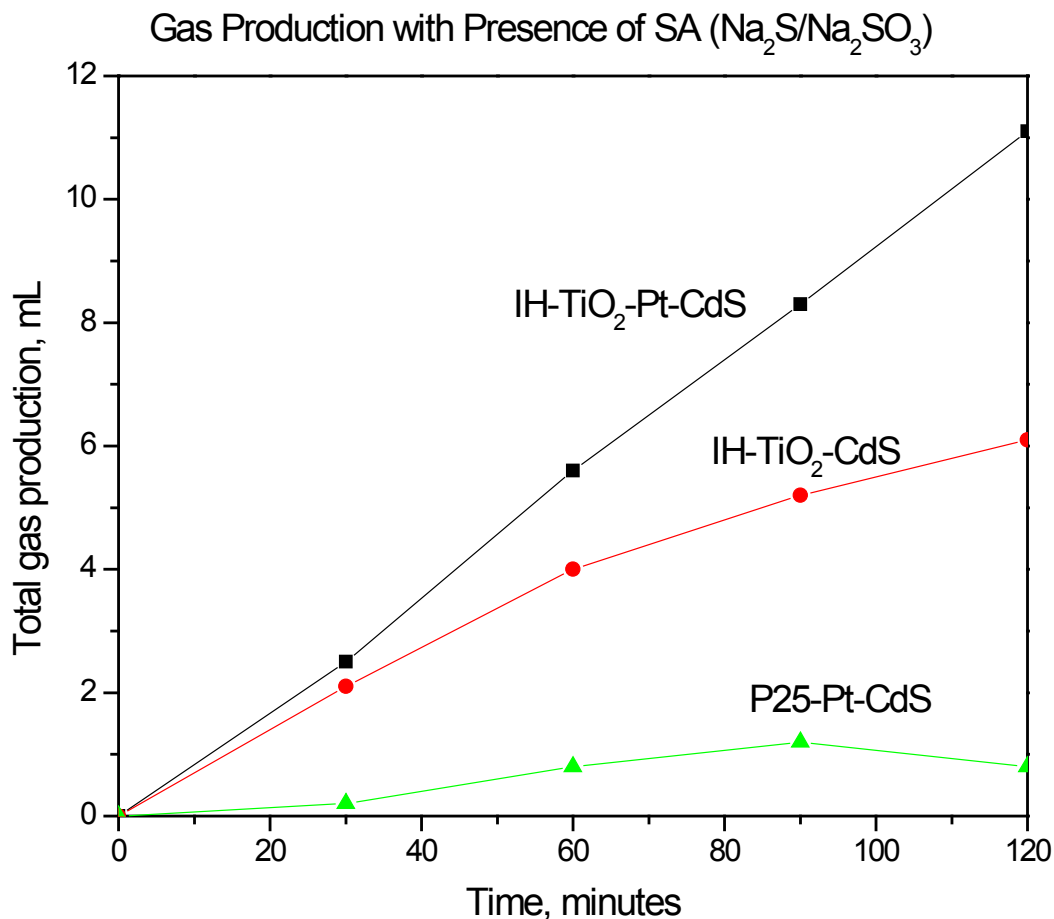
# Barrier 3 – Fuel+waste (Optical properties)

- The IH  $\text{TiO}_2$  allows for greater deposition of CdS (due to higher surface area)
- The absorbance ( of CdSe) is also noticed to increase farther into the visible part of the solar spectrum



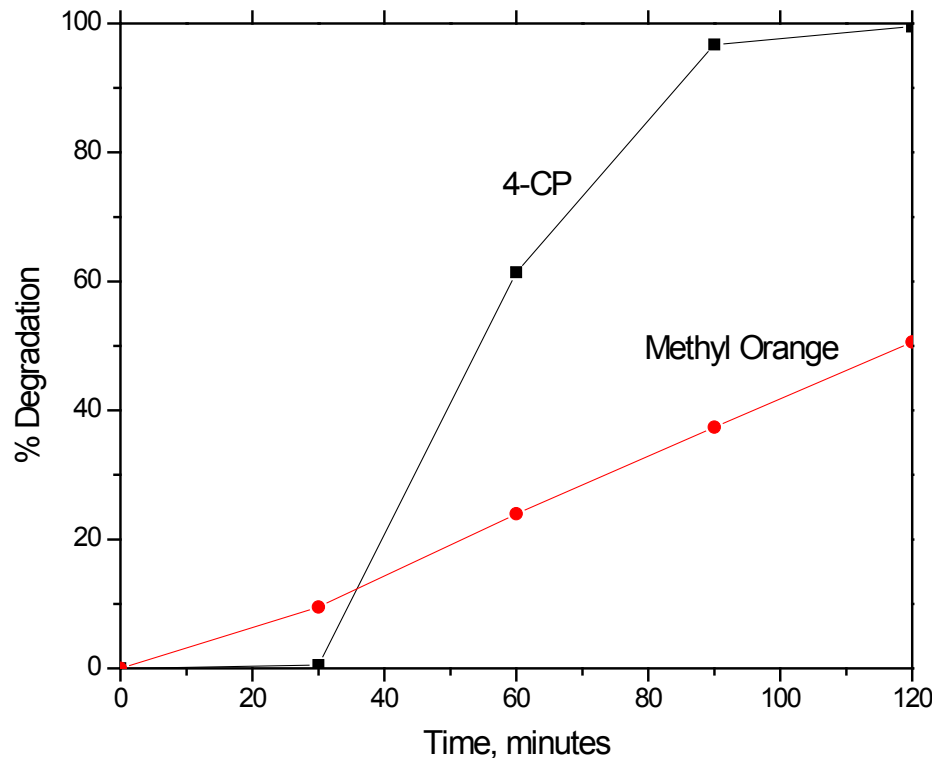
# Barrier 3 – Fuel+waste ( $H_2$ generation data)

- The IH-TiO<sub>2</sub>-Pt-CdS photocatalyst shows the maximum hydrogen yield
- The electrolyte has counter sulfide ions to maintain the stability of CdS



# Barrier 3 – Fuel+waste (Photodegradation)

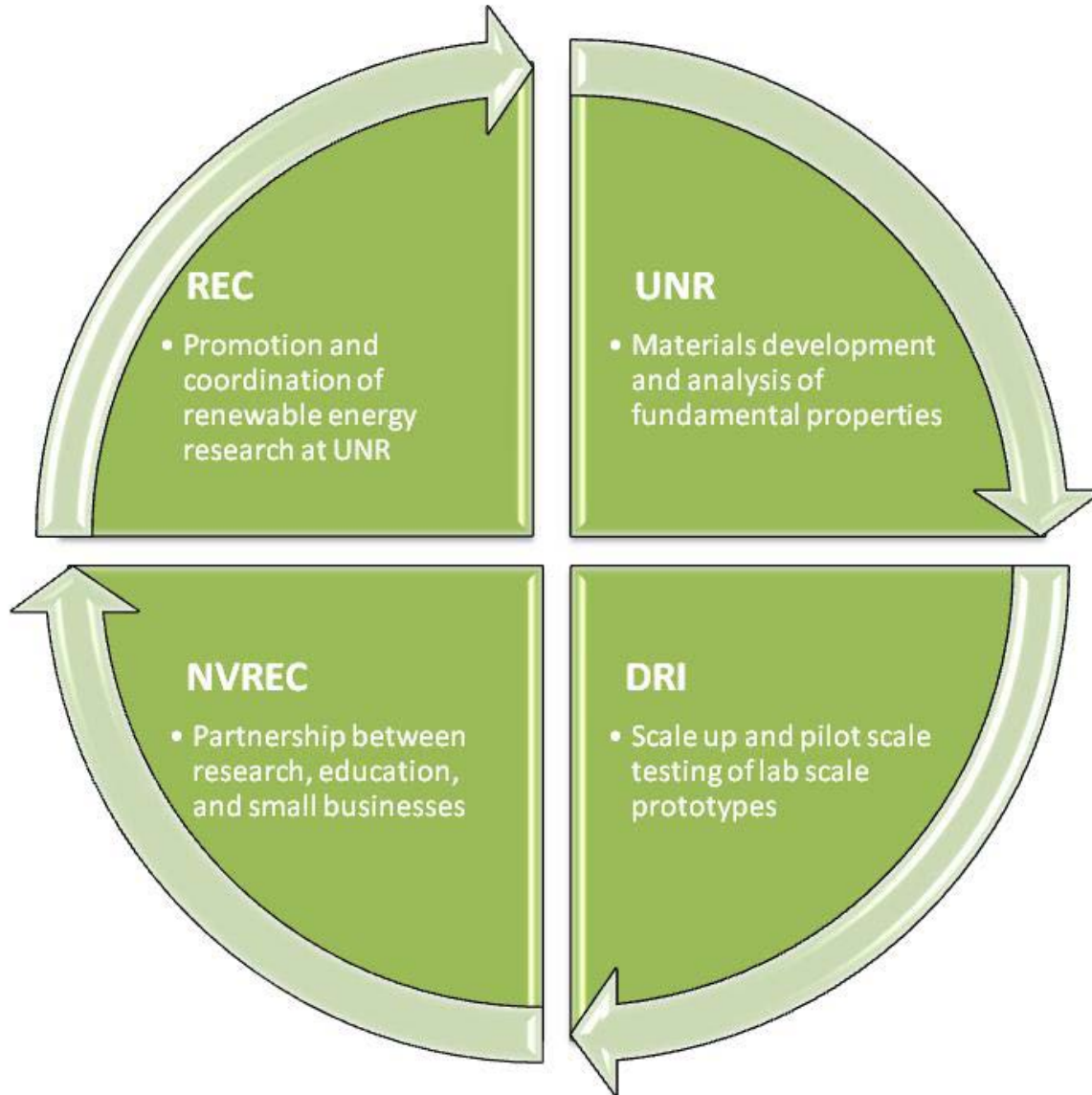
- The addition of pollutants such as methyl orange or 4-chlorophenol shows pollutant degradation indicating a synergistic activity of the photocatalyst
- How does this assist with hydrogen generation?
- What is the stability of the photocatalyst?





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# Collaborations





# Summary

- ❑ Relevance – Examine feasibility of
  - ❑ synthesizing nanotubes efficiently,
  - ❑ depositing visible light harvesting material effectively, and
  - ❑ testing hydrogen generation and photodegradation – simultaneously.
- ❑ Approach – Proof-of-concept has been demonstrated using
  - ❑ low volume solvent for nanotube synthesis and
  - ❑ solvothermal process for CdS deposition.
- ❑ Technical accomplishments – Results suggest that
  - ❑ T<sub>NT</sub> nanotubes can be synthesized effectively using a reduced electrolyte volume.
  - ❑ solvothermal is a good technique to deposit and pack light harvesting chalcogenide.
  - ❑ Preliminary data indicates hydrogen production and photodegradation could be possible simultaneously.
- ❑ Collaboration
  - ❑ DRI – Alan Gertler
  - ❑ UNR – Ravi Subramanian