SYNTHESIS OF TiO_2-CdS PHOTOCATALYST & STUDYING ITS PHOTOCATALYTIC ROLE FOR: (i) CARBAMAZIPINE DEGRADATION & (ii) WATER SPLITTING, UNDER SOLAR & UV RADIATION

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Motivation & Relevance to Research

The existing technologies that are employed on wastewater treatment plants are found to be insufficient as far as the treatment of a rapidly growing newer contaminants such as pharmaceuticals, dyes, and several other industrial chemicals are concerned. In particular, the carbamazepine (CBZ), one of the common antidepressant that is only 52% metabolized by human body, showed insignificant degradation on UV treatment. However, preliminary results in our lab have shown effective degradation under UV activated TiO2 photocatalyst. In this project, we synthesized the novel CdS-TiO2 photocatalyst that is believed to be capable of utilizing a broader visible range of solar light by the process called Inter-particle charge transfer (IPCT) to drive the more efficient *redox reaction* that produces *advanced oxidative degradation of carbamazepine*. In addition, a renewable & inexpensive method of H_2 production by *photocatalytic splitting of water* by this photocatalyst will also be studied. The trade off between these two functions of this visible-active photocatalyst will be optimized.

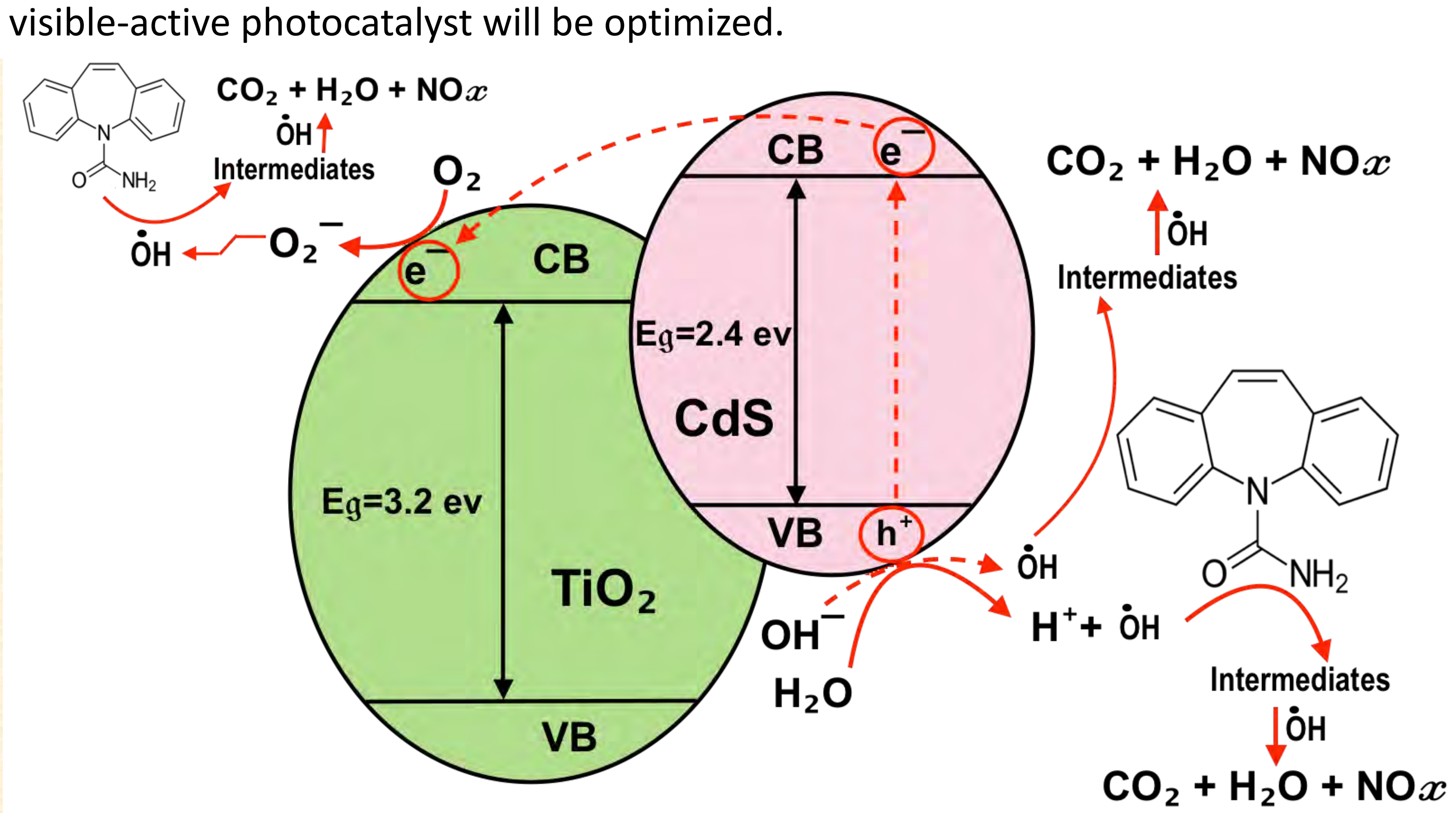

Fig 1.: Schematic showing photocatalytic degradation of CBZ by visible light activated TiO2-CdS photocatalyst

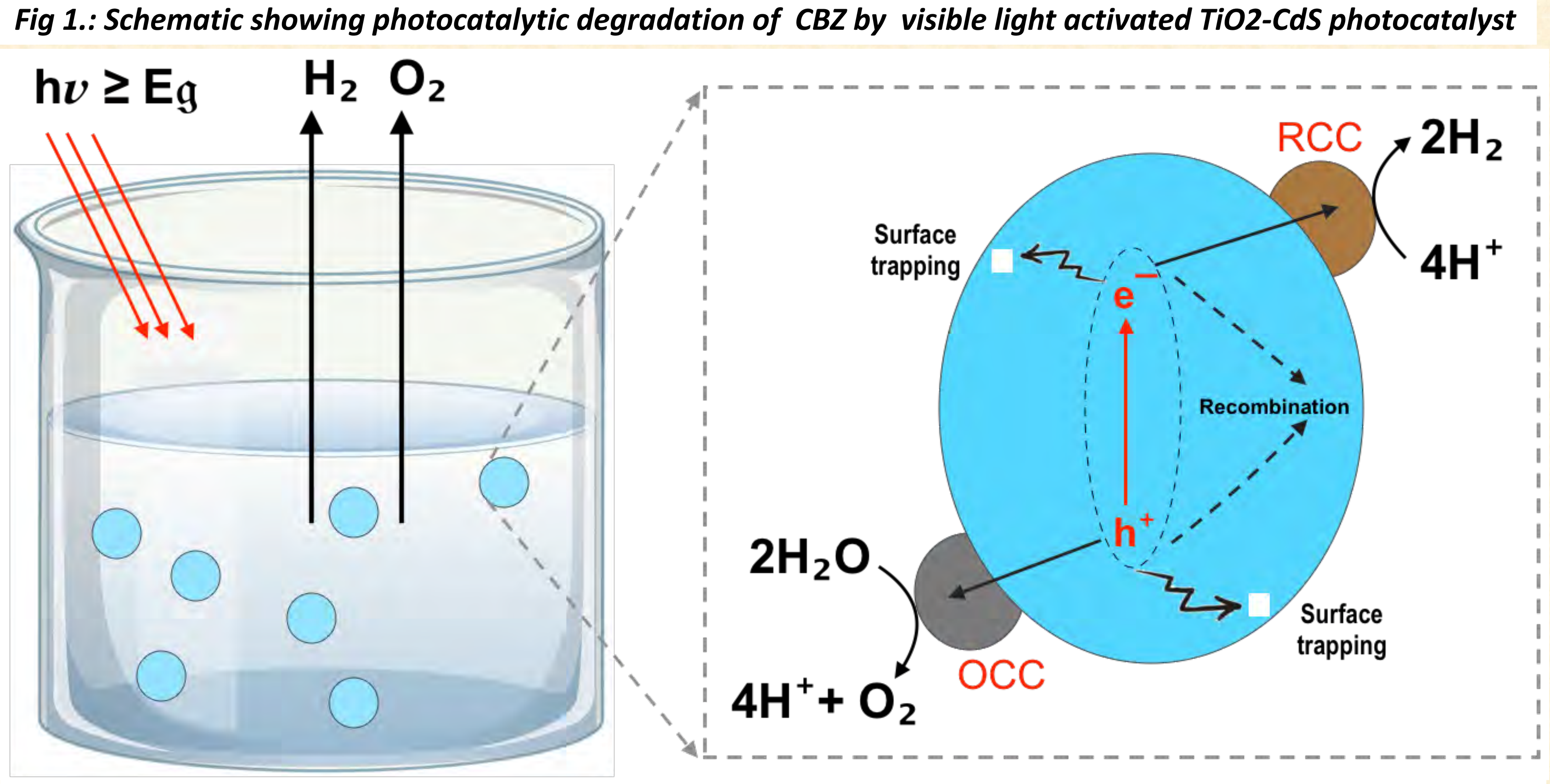

Fig 2.: Schematic showing production of hydrogen energy by photocatalytic splitting of water

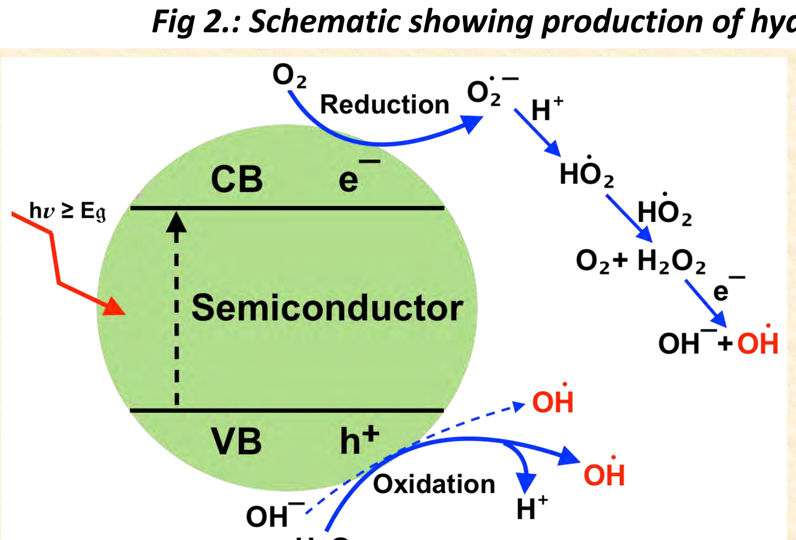

Fig 3.: Photocatalytic formation of hydroxyl free radical

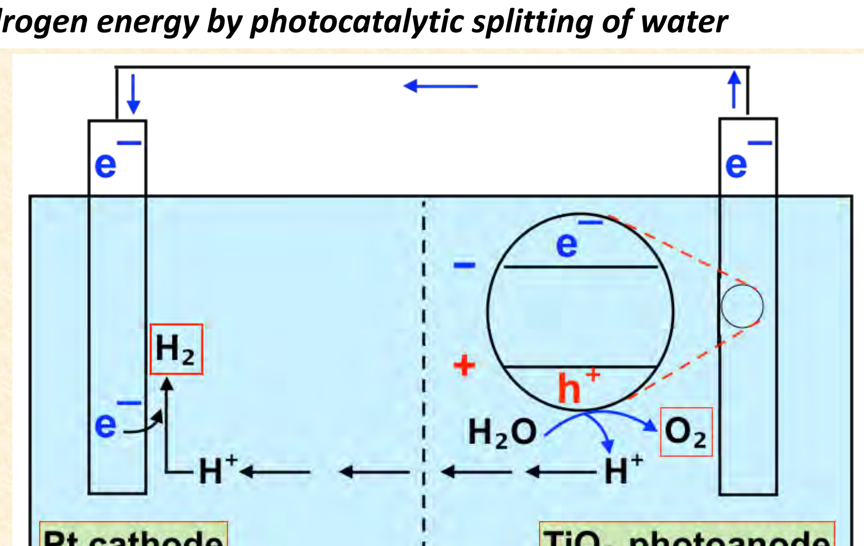

Fig 4: Photoelectrocatalytic water splitting for H_2 production

Project Objectives

	To develop a general technique to synthesize TiO2-CdS photocatalyst for:
1	Carbamazepine degradation • Testing degradation rates under various experimental conditions • Proposing a general reaction mechanism and global reaction kinetics • Evaluation of overall efficiency of this photocatalyst for this purpose
2	Hydrogen production by photocatalytic water splitting • Testing H_2 production rates under various experimental conditions • Proposing a general reaction mechanism and global reaction kinetics • Evaluation of overall efficiency of this photocatalyst for this purpose
3	• Developing an optimized operating conditions for its dual function

Methods & Methodology

Sol-Gel synthesis of TiO2 nanoparticles using titanium isopropoxide precursor

1. Sol formation by hydrolysis of the precursor:

- Dissolve titanium isopropoxide (precursor) in alcohol (e. g. ethanol)
- Mix the solution in water followed by vigorous stirring that causes hydrolysis of the precursor forming titanium hydroxide (sol form)

$$\boldsymbol{Ti}\,[\boldsymbol{OCH(CH_3)_2}]_4 + 4H_2O \rightarrow \boldsymbol{2Ti(OH)_4} \downarrow + 4(CH_3)_2CH - OH$$

2. Gel formation by condensation of the Sol:

- Condensation of titanium hydroxide (sol) forms the TiO_2 (gel)

Water condensation

$$\boldsymbol{Ti(OH)_4} + \boldsymbol{Ti(OH)_4} \rightarrow \boldsymbol{2TiO_2} \downarrow + 4H_2O$$

Alcohol condensation

$$\boldsymbol{Ti(OH)_4} + Ti\,[OCH(CH_3)_2]_4 \rightarrow \boldsymbol{2TiO_2} \downarrow + 4(CH_3)_2CH - OH$$

3. Aging of the Gel:

- Over the time, polycondensation occurs that increases the 3-D gel network

4. Drying & Calcination:

- Gel is subjected to drying at ambient condition for a long time or calcined between 400 to 800 ^{0}C to obtain powder nanoparticles of TiO2

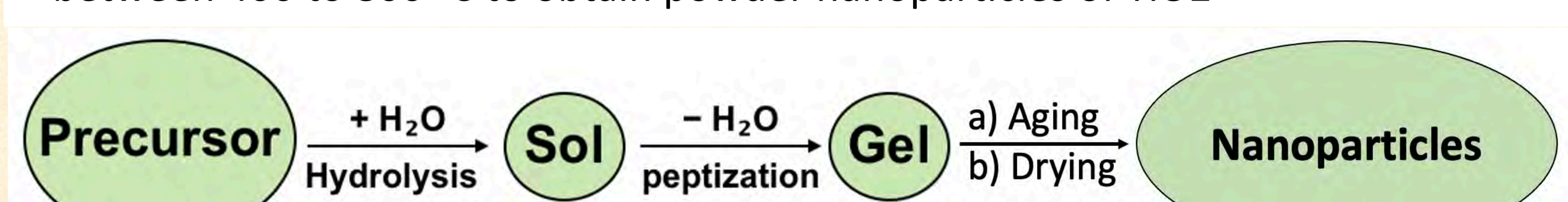

Fig 5: Sol-gel process for formation of TiO2 nanoparticles

In-situ synthesis of aqueous. suspension of CdS nanoparticles

- Mixing aqueous solution of cadmium nitrate tetrahydrate & sodium sulfide nonahydrate followed by mild stirring for 15 minutes at 25^{0}C

$$Cd\,(NO_3)_2.4H_2O(aq) + \boldsymbol{Na_2S.9H_2O(aq)} \rightarrow \boldsymbol{CdS} \downarrow + \boldsymbol{2NaNO_3(aq)} + \boldsymbol{13H_2O}$$

Add TiO_2 nanoparticles into the above mixture

- At this point, the mixture contains undissolved CdS, undissolved TiO_2, dissolved $NaNO_3$ in water

$$CdS \downarrow + TiO_2 \downarrow + 2NaNO_3(aq) + 13H_2O$$

Recovery of the synthesized TiO2-CdS photocatalyst from the mixture

- Mild stirring in magnetic stirrer for 20 hours at 25^{0}C for uniform mixing.
- Filter the mixture, wash the residue multiple times with distilled water , & discard the filtrate
- Collect the resulting composite photocatalyst particles (CdS-TiO_2)
- Let it air dry at room temperature (25^{0}C) for 24 hrs.
- This composite photocatalyst powders are crushed & stored in the dark.
- It is ready to use at any time.

Fig 6: Lab scale synthesized TiO2-CdS photocatalyst

Experimental & Instrumentation

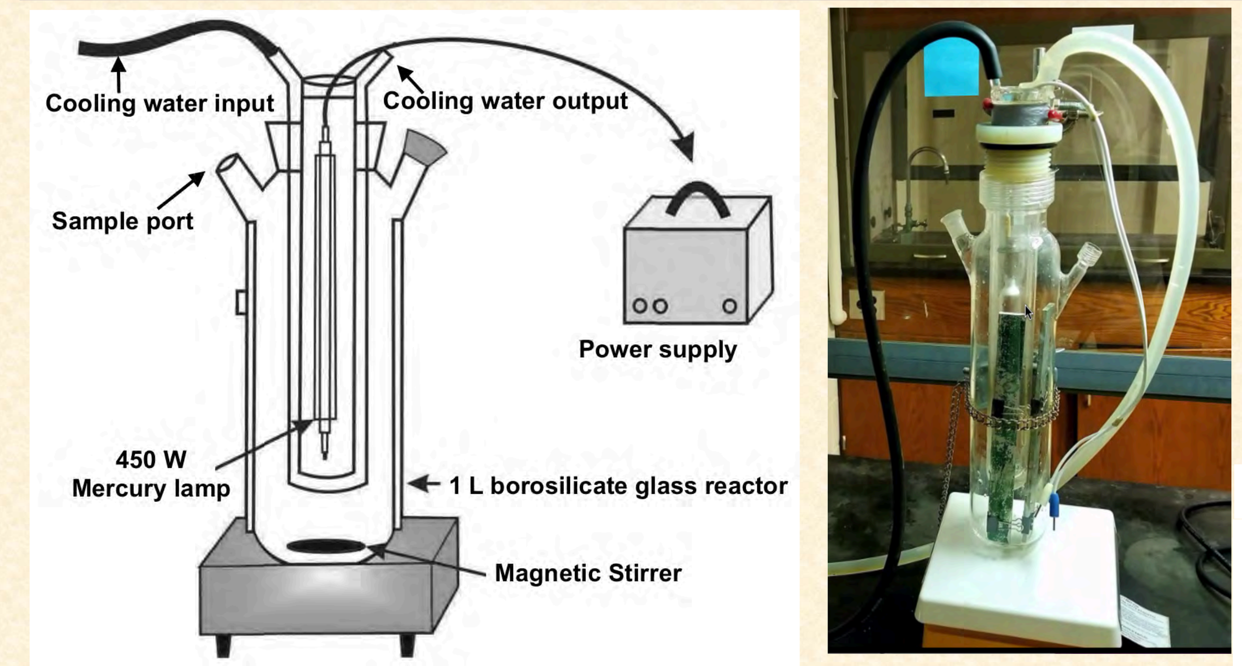

Fig 7: Photocatalytic reactor; a) Schematics, b) One in Dr. Arce's lab (PH 353)

Fig 8. UV/Vis spectrophotometer

$$T = I/I_0$$
$$A = -\log T = \log(1/T)$$
$$\Rightarrow A = \log(I_0/I)$$

Analysis

Using the UV/Visible Spectrophotometer, absorbance by the sample is measured, and by applying the Beer-Lambert's equation, the concentration of the sample is determined:

$$A = \epsilon c l \Rightarrow c = \frac{A}{\epsilon l} \Rightarrow c_0 = \frac{A_0}{\epsilon l};\ \&\ c_t = \frac{A_t}{\epsilon l} \Rightarrow \frac{C_t}{C_0} = \frac{A_t}{A_0} \Rightarrow C_t = C_0\frac{A_t}{A_0}$$

- C_t: Conc of **CBZ left undegraded** at time "t"
- C_0: Initial conc of CBZ, i. e. CBZ concentration before the rxn started (known value)
- A_0: Absorbance by CBZ before the reaction started (read from spectrophotometer)
- A_t: Absorbance by CBZ at "t" (read from spectrophotometer)
- % of the CBZ conc degraded photocatalytically at time "t" is given by:

$$\%\,Degradation = (1 - C_t/C_0) \times 100$$

Results & Future Work

- TiO2-CdS composite photocatalyst was successfully synthesized in the laboratory for performing the experiments
- Characterization of this photocatalyst will be done: (i) particle size using Dynamic Light Scattering (DLS) and (ii) XRD for elemental analysis.
- Suspension based photocatalytic degradation studies of carbamazepine will be performed in UV and Visible lights using photocatalytic reactor present in Dr. Arce's lab (PH 353)
- The progress of the reaction will be analyzed using Spectrophotometer (Dr. Sanders' lab, Prescott 401)
- Coating-based continuous process for CBZ degradation will be performed in lab scale and the results will be upscaled and eventually implemented in practice.
- Photocatalytic water splitting for H_2 generation using Platinum doped TiO2-CdS will be studied.

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