44th International Conference on Environmental Systems

Visible-Light-Responsive Catalysts Using Quantum-Dot Modified TiO_2 for Air and Water Purification

Dr. Janelle L. Coutts	KSC, Engineering Services Contract
Dr. Paul E. Hintze	KSC, NASA NE-L Directorate
Dr. Christian A. Clausen	University of Central Florida, Dept. of Chemistry
Mr. Jeffrey T. Richards	KSC, Engineering Services Contract

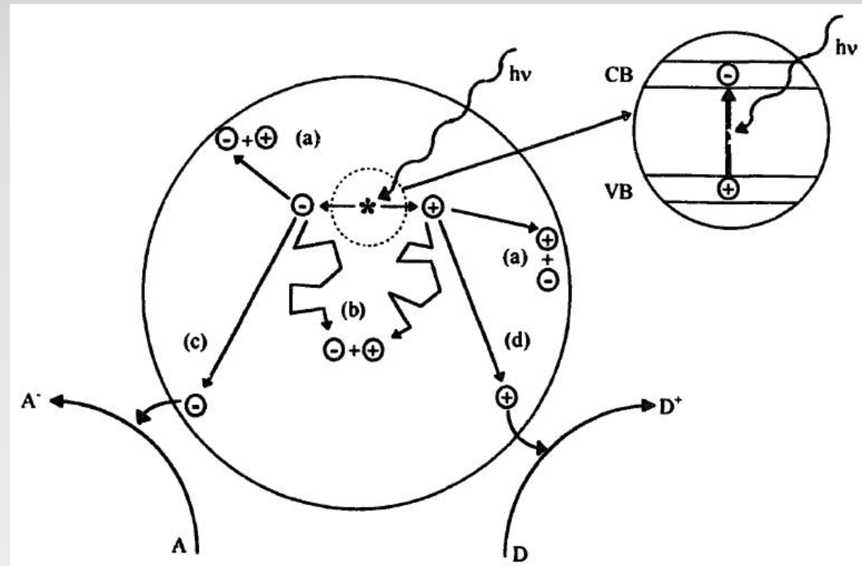
Marriott University Park, Tucson, AZ

July 13-17, 2014

Background & Project Goals

Photocatalysis

- Titanium dioxide has dominated the field for decades
  - Commercially available Degussa P25
    - 70-85% anatase, 15-30% rutile
    - 3.2 eV band gap for anatase requires photons of 388 nm or lower (UV) for activation
  - Traditional Hg-vapor light sources precludes use in crewed spacecraft
  - Photonic energy requirements disallow use of indoor lighting or majority of solar spectrum
  - Only provides moderate reaction rates
  - Somewhat low quantum yield



Processes occurring in a photocatalyst after electron-hole separation (Agrios et al. 2003):
(a) Recombination of the electron and hole at the surface
(b) Recombination of the electron and hole on the bulk of the material
(c) Electron participation in the reduction reactions
(d) Hole participation in oxidation reactions

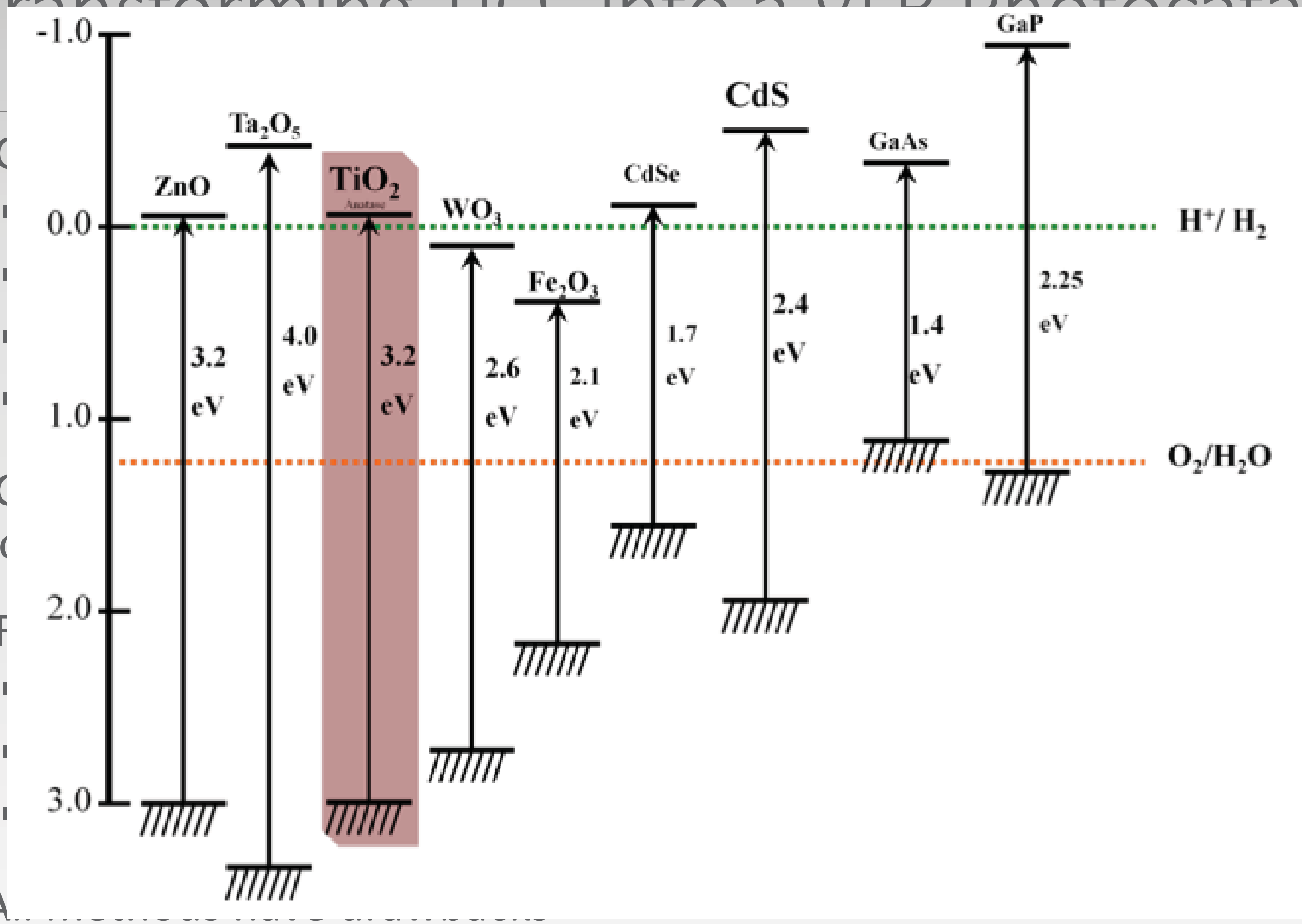
Visible-Light-Activated Photocatalysis

- Possible solution to photocatalysis limitations: enable TiO_2 to become visible light responsive (VLR)
  - Allows for use of better use of solar radiation (~45% of the spectrum lies in the visible region)
  - Allows for use of highly efficient blue or white LEDs
  - Can lower electron-hole recombination events
- Applications include:
  - ISS applications
    - Air Trace Contaminant Control (TCC)
    - Water recovery systems
  - Low-cost H_2 production using solar energy
  - Enhanced chemical and microbial purification of water
- How do we achieve this?

44th International Conference on Environmental Systems

Transforming TiO_2 into a VLR Photocatalyst

- C
- C ... k of co
- F
- A... methods have drawbacks



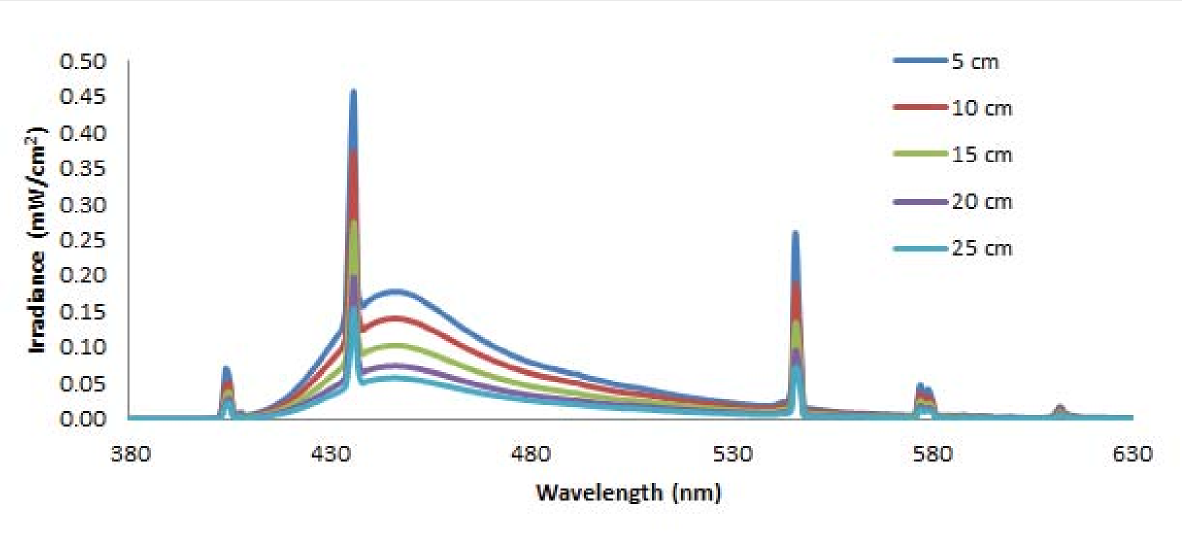
Project Goals

- Development of a VLR-TiO_2 catalyst library focused on coupling narrow band gap semiconductors with TiO2 via:
  - Photodeposition
  - Mechanical alloying
- Development of rapid screening methods in both aqueous and gas phase for consistent evaluation of each catalyst
- Comparison of catalysts prepared in-house and commercially available VLR catalyst systems

Methods & Materials

Light Source Characterization

- Custom light bank of six 24-W Marine Glo T5 high output fluorescent bulbs utilized throughout this study
- Irradiance profiles at varied distances determined in a dark room using an Optronics Laboratories OL754C spectroradiometer
  - Sharp peaks at 404, 435, 546, 578 are due to emission lines from mercury
  - Broad peak from ~400 to 500 nm due to phosphor coating on the wall of the lamp
- Height with highest irradiance used for both aqueous and gas phase studies



Catalyst Preparation

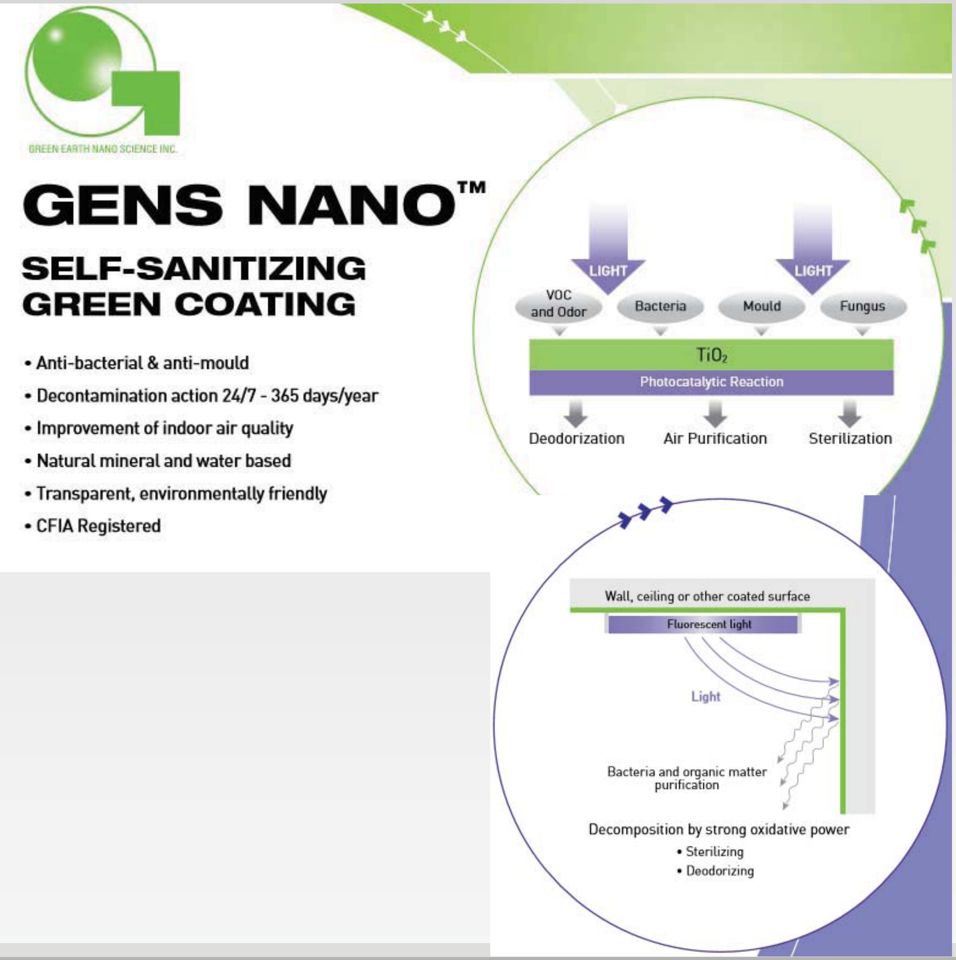
- 45 catalysts prepared by two methods: photodeposition or mechanical alloying
  - Degussa P25 TiO_2 coupled with metal sulfide quantum dots, metal selenide quantum dots, and/or pure metal
  - Photodeposition formed quantum dots on TiO_2 surface using UV radiation and metal salts/sulfur quantum dot precursors
  - Mechanical alloying milled TiO_2 with purchased quantum dots

Left: Photodeposition preparation method for quantum dot formation on TiO_2

Right: Spex 8000M Mill used for mechanical alloying

Commerical VLR Catalyst

- GENS NANO Solution
  - Claims to allow treated surfaces to be self-sanitizing and self-cleaning
  - Proprietary altered TiO_2 formula that harvests solar or fluorescent light energy to activate catalyst
  - Sold as an aqueous sol solution to be applied to surfaces



Rapid Aqueous Phase Assay

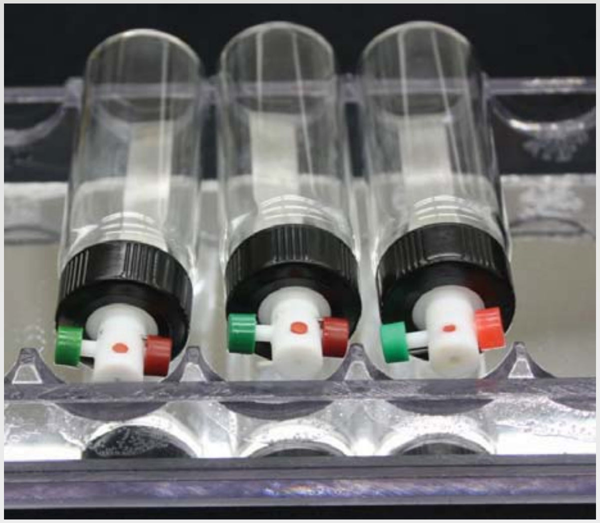
- 4-chlorophenol (4CP) test contaminant
- Catalyst loading rate: 10 mg/mL contaminant solution
- All reactions carried out in a Controlled Environment Chamber (CEC) at 30°C
- Dark adsorption for 30 min followed by visible light irradiation for 30 min with stirring
- Analysis via HPLC for 4CP removal:

$$Removal\ \% = \left(\frac{[4CP]_{Initial} - [4CP]_{Final}}{[4CP]_{Initial}}\right) * 100$$

Catalyst samples prepared for Liquid Assay

Liquid assay setup

Rapid Gas Phase Assay

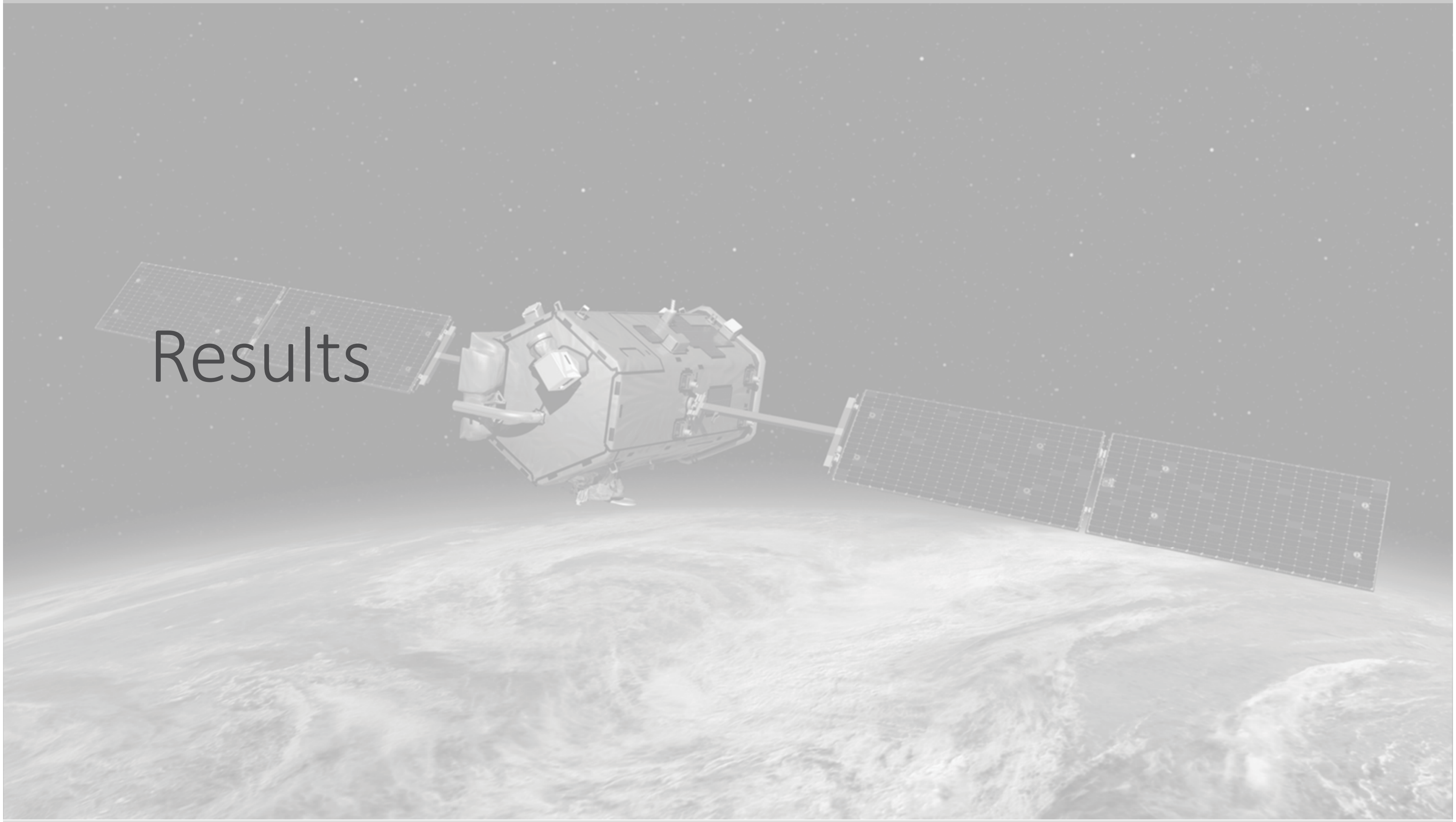


Gas assay setup

- Ethanol test contaminant
- 5 mg/mL aqueous catalyst slurry deposited on aluminum coupons to create thin film
- Dark adsorption for 60 min followed by visible light irradiation for 60 min
- Analysis via GC-FID for ethanol removal and acetaldehyde formation
- Assay designed to be rapid; not optimized for completed mineralization of EtOH to CO_2

Catalyst Characterization

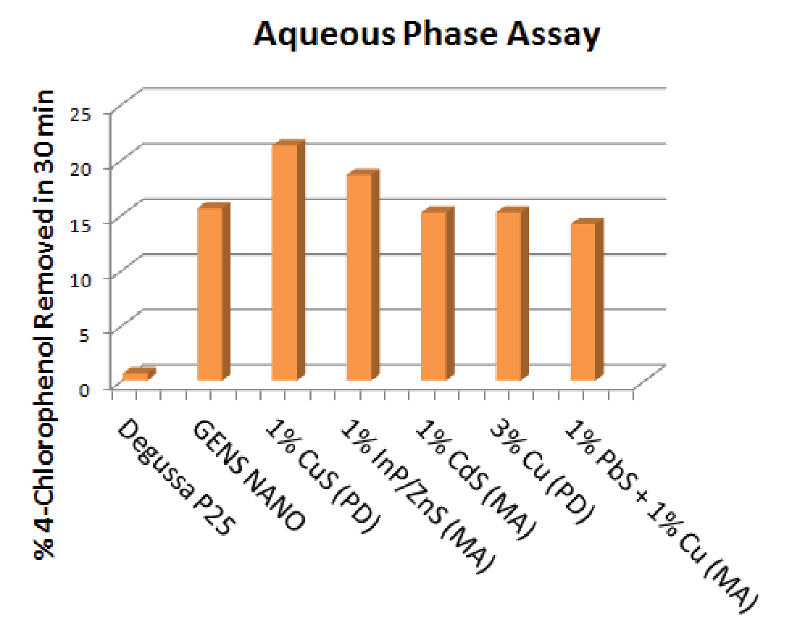
- Diffuse Reflectance Analysis
  - Jasco V-670 UV/Vis spectrophotometer equipped with 60-mm diameter integrating sphere
  - % reflectance from 300-800 nm
  - Reference material: Spectralon (Labsphere)
- X-Ray Photoelectron Spectroscopy (XPS) Analysis
  - Thermo Scientific K-Alpha system
  - Completed for catalysts with appreciable VLR activity
  - Comparison for catalysts prepared via both methods



Results

Rapid Aqueous Phase Assay

- 5 catalysts with 0.4%+ per min degradation rates of 4CP
- Degussa P25 exhibited minute activity likely due to small % of UV emitted from light source
- GENS NANO out performed by 2 in-house catalysts
  - Other in-house catalysts showed near-equivalent performance

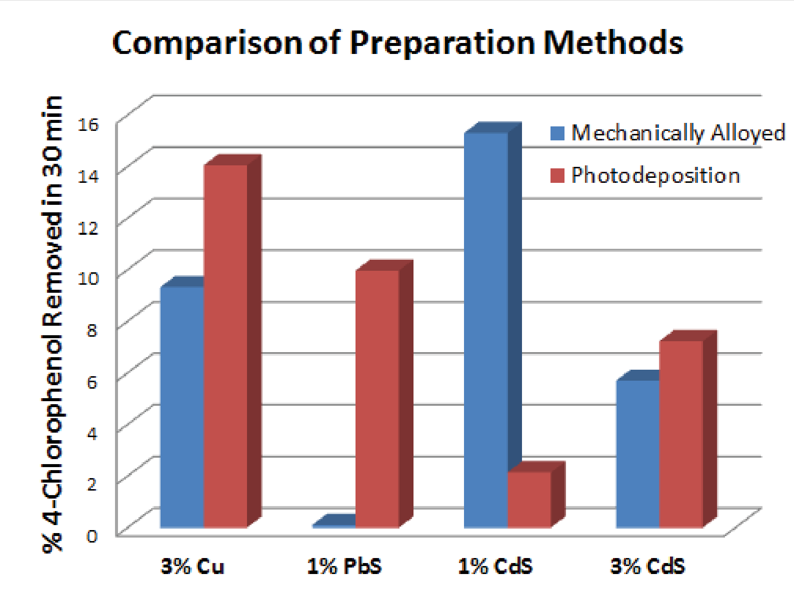


4CP removal capacity of top-performing catalysts for aqueous phase assay.

PD = photodeposition method
MA = mechanical alloying method

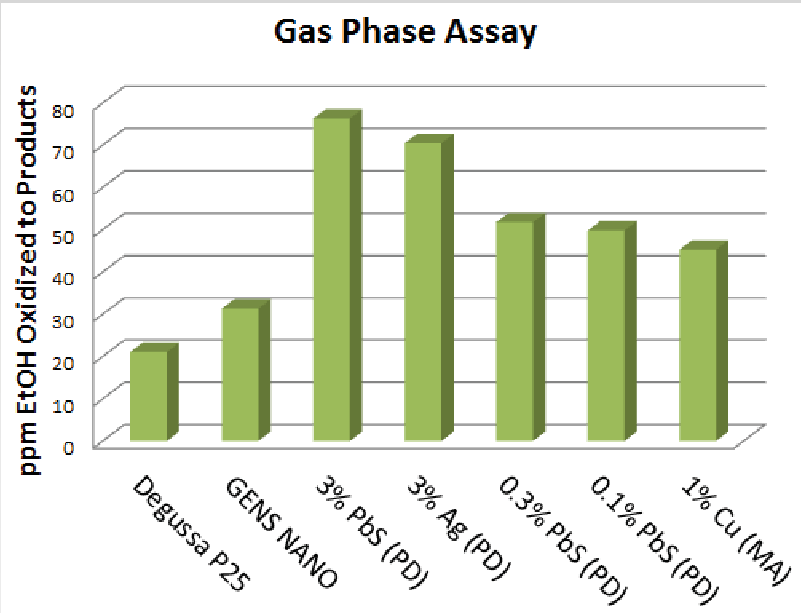
Rapid Aqueous Phase Assay

- Neither preparation method proved more successful than the other in the current experiment
- Requires further investigation into preparation method relationship with catalyst activity
  - Mechanical alloying method, if determined to be favored, is a faster process
  - Photodepositon followed by mechanical alloying may further increase activity by increasing catalyst surface area.



Aqueous assay results with respect to comparison method

Rapid Gas Phase Assay

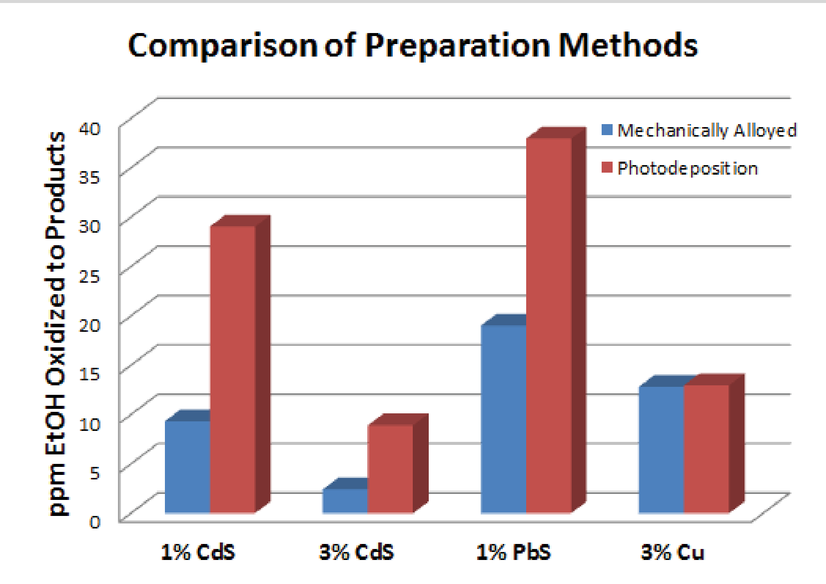


4CP removal capacity of top-performing catalysts for gas phase assay.

PD = photodeposition method
MA = mechanical alloying method

- 5 top-performing catalysts for photocatalytic oxidation of ethanol to acetaldehyde
- Degussa P25 found to have ~18% removal even with polyacrylic UV filter in place
  - 100% of UV exposure was not omitted
- GENS NANO showed improvement over bare TiO2 but not near the activity of in-house catalysts
- Acetaldehyde is not a favored product
  - Constraints on reactor design limited analytical methods
  - Still serves as worthwhile indicator of catalyst activity

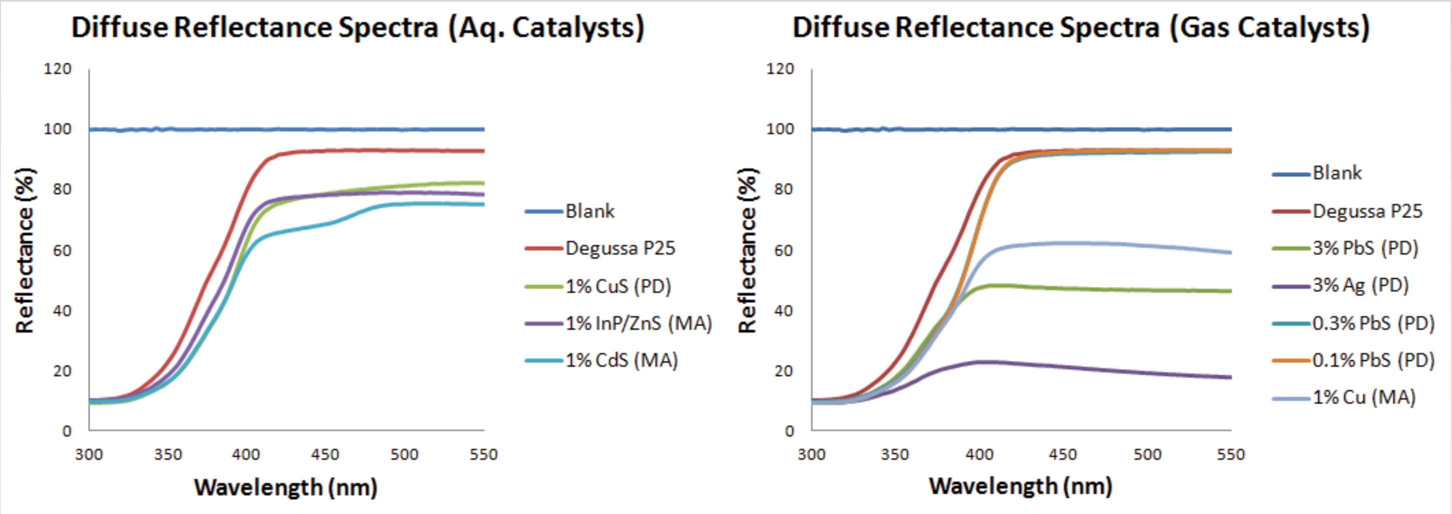
Rapid Gas Phase Assay



Gas assay results with respect to comparison method

- Comparison of preparation methods shows clear difference in activity
- Photodeposition method proved superior to mechanical alloying method
- Could be due to oxidation of the metal and/or quantum dot species during mechanical alloying process
- XPS analysis showed definitive differences in metal and/or quantum dot peaks for the alternate preparation methods
  - E.g.: PbS-modified sample showed intact PbS peak for photodeposition method but was altered in the mechanically alloyed sample
  - Shows drawback of high-energy, high-temperature reactions

Diffuse Reflectance Analysis



- Diffuse reflectance data allows for calculation of material's band gap energy
- For all samples analyzed, there is a clear red-shift in the reflectance shoulder
  - Explains increased activity in visible region over Degussa P25
- Degussa P25 shows two shoulders (anatase and rutile phase)
- Several samples also exhibit multiple shoulders (TiO_2 and other metal or quantum dot)

Conclusions & Future Work

- Project Achievements:
  - Development of rapid assays for close the intellectual gap in current research
  - Promising initial results for multiple in-house developed catalysts in both gas and liquid phase assays
  - In-house catalysts with performance rates far above a commercially available VLR catalyst
  - Further development can lead to many applications for ISS, future space exploration systems, and terrestrially.
- Results support a need for further investigation into top-performing catalysts
  - Closer comparison of preparation methods
  - Optimization of catalysts
  - Further assays studying recalcitrant target compounds

Acknowledgements

The authors would like to thank:

- The late Dr. Lanfang Levine, KSC Engineering Services Contract
- Dr. Steven Trigwell, KSC Engineering Services Contract
- Lawrence Koss, KSC Engineering Services Contract
- Dr. Thomas Graham, KSC NASA Postdoctoral Program
- Dr. Phillip Maloney, KSC NASA Postdoctoral Program

Research support was provided by the Kennedy Space Center 2011 Center Innovation Fund (CIF)

Questions?