Synthesis and Application of Nanosize Semiconductors for Photoxidation of Toxic Organic Chemicals

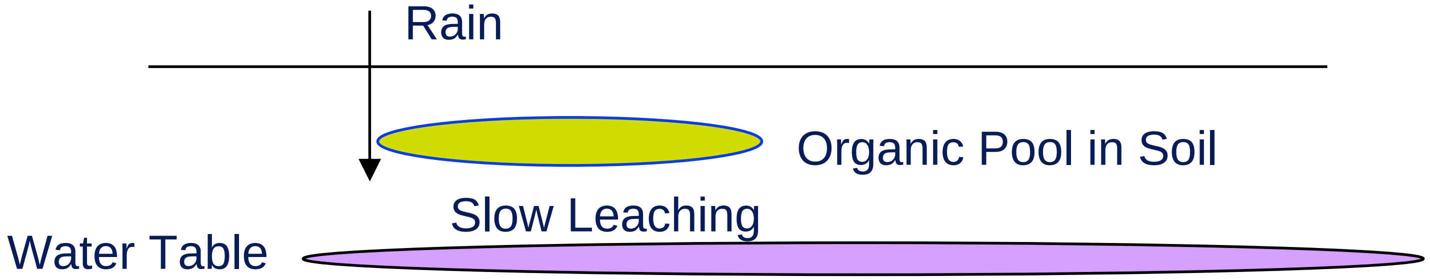
J.P. Wilcoxon,
Nanostructures and Advanced Materials Chemistry
Sandia National Laboratories
Albuquerque, N.M., 87185-1421
jpwilco@sandia.gov
Colloborators: T.R. Thurston, P. Provencio, G.A. Samara

Talk Outline

- Industrial Solvents in the Environment (Impregnated Sediments, Water Table)
- Brief History of the problem and possible remediation approaches (Bioremediation, Soil Washing, Adsorption, Photooxidation)
- Photocatalysis using UV light and nanosize TiO_2 and SnO_2.
- Photocatalysis using visible light and MoS_2 nanoclusters.

- *Acknowledgement: Div. Of Materials Science and Engineering, Office of Science, US Dept. of Energy under contract DE-AC-04-AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the US Dept. of Energy. This work performed under the aupices of the DOE Environmental Science/Environmental Research (ER/ES) Program.*

Typical Scenario-Dense Non-Aqueous Solvent Pools



- Examples-
- Cleaning Solvents- Tri-Chloroethylene (TCE)
- Herbicides/Fungacides/Pesticides (Pentachlorophenol (PCP), DDT)
- Explosives (e.g. TNT)

- Major Remediation Issues-
- 1) Low Solubility (1-10 ppm) in water provides continuous leaching with time
- 2) Treatment of large volumes of highly diluted toxins
- 3) Cost of treatment

Possible Treatment Approaches-

Step 1: Excavation, Soil Washing

Conventional Treatment Options:

1)Filtration and/or Adsorption of toxic chemicals in aqueous supernatant from Step 1

2)Chemical Oxidation or Total Mineralization of the the Organics

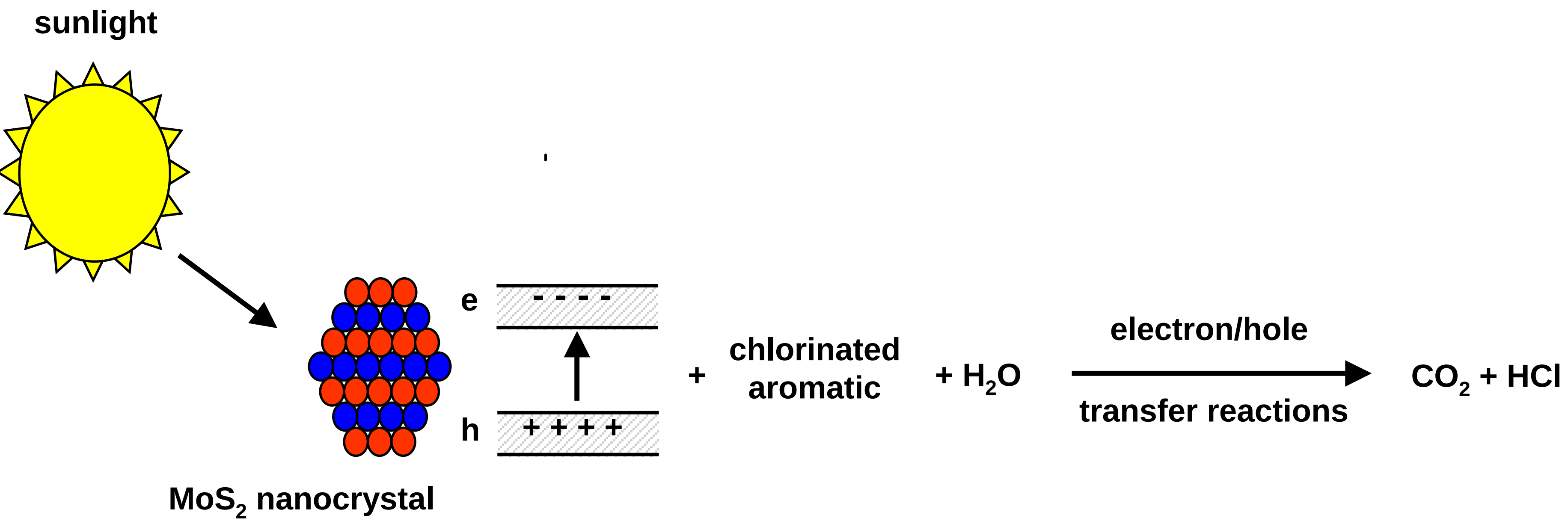
3)Deep UV Photooxidation of the Organics

4)Photocatalytic oxidation of the Organics (e.g. colloidal titania slurries)

- *Cost and large volumes involved are the principal practical concerns.*

Alternative Approach

Use stable, inorganic, semiconductor nanoclusters with tunable bandgaps to oxidize organic chemicals using sunlight



- *Clusters can be used in both dispersed and heterogeneous forms (supported)*

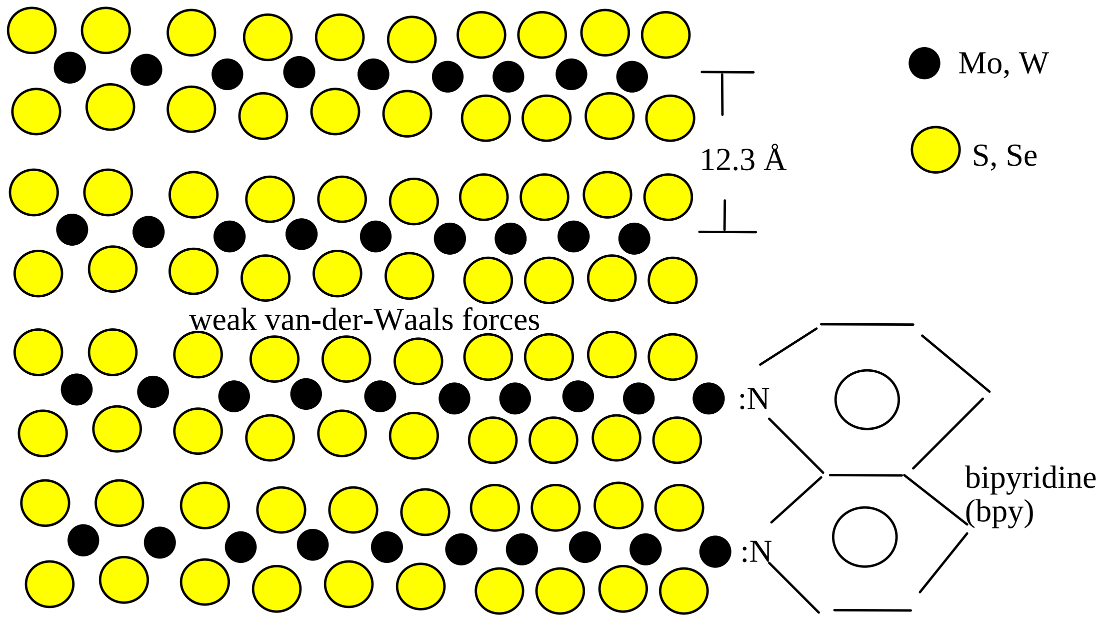
Advantanges of this Approach-

- The light absorption and energy levels of the semiconductor valence and conduction bands can be adjusted in a single material by changing the size (quantum confinement effect).
- A covalent semiconductor material with excellent photostability and low toxicity can be selected (e.g. MoS_2).
- Our synthesis allows easy chemical modification of the nanocluster surface properties (e.g. deposition of a metal).
- Small size of nanocluster vastly reduces electron-hole recombination rate and undesired light scattering.
- Nanoclusters are easily deposited on bulk support materials from a dispersed liquid phase.
- Both dispersed and supported nanoclusters can be studied, allowing complete characterization of the photocatalyst microstructure.

Photocatalysts Material Requirements -

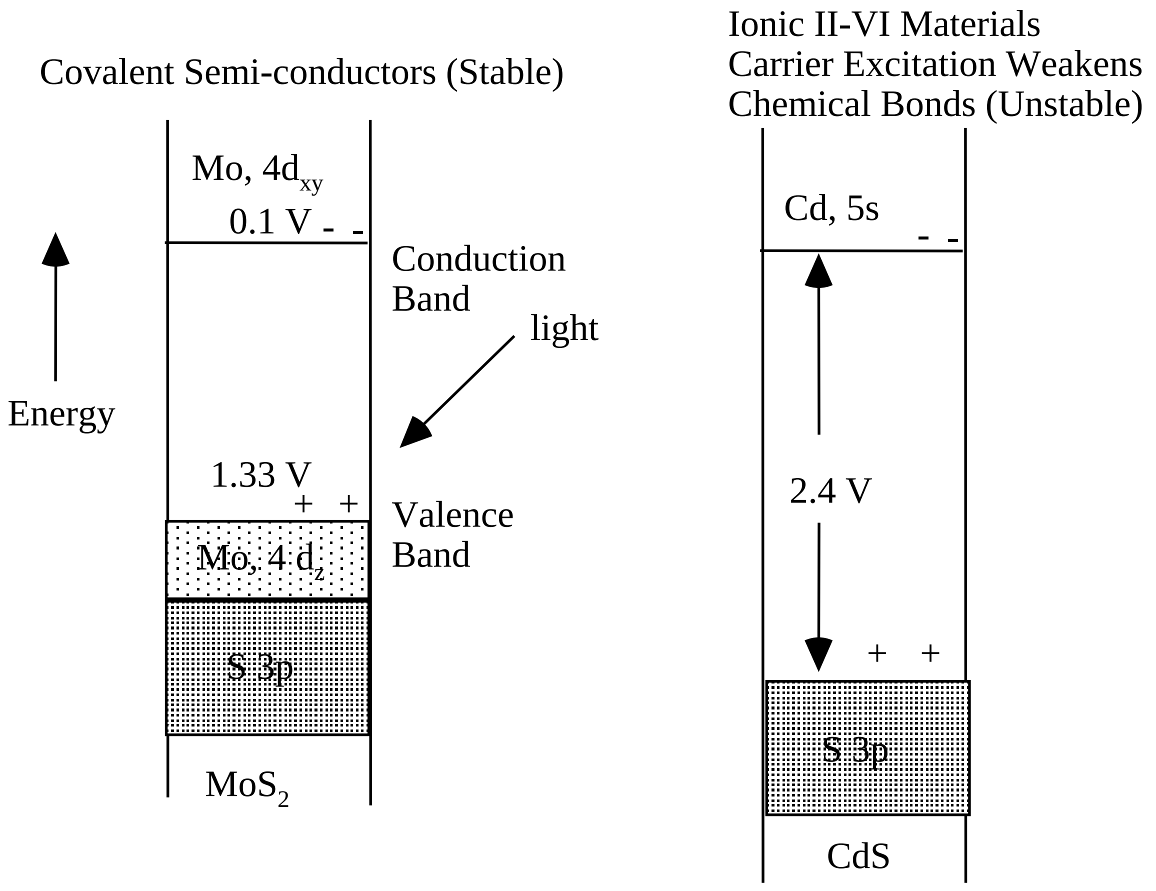
1) Efficient conversion of sunlight to electron-hole pairs.
2) Surface trapping of electrons and holes before recombination.
3) Catalyst photostability.
4) Inexpensive, chemically-stable, environmentally benign materials.

MoS_2 layered structure gives chemical stability-



- Binding of substrate organic chemical occurs at metal edge sites.
- Electron transfer rates allow an estimation of shift of the redox potential with size

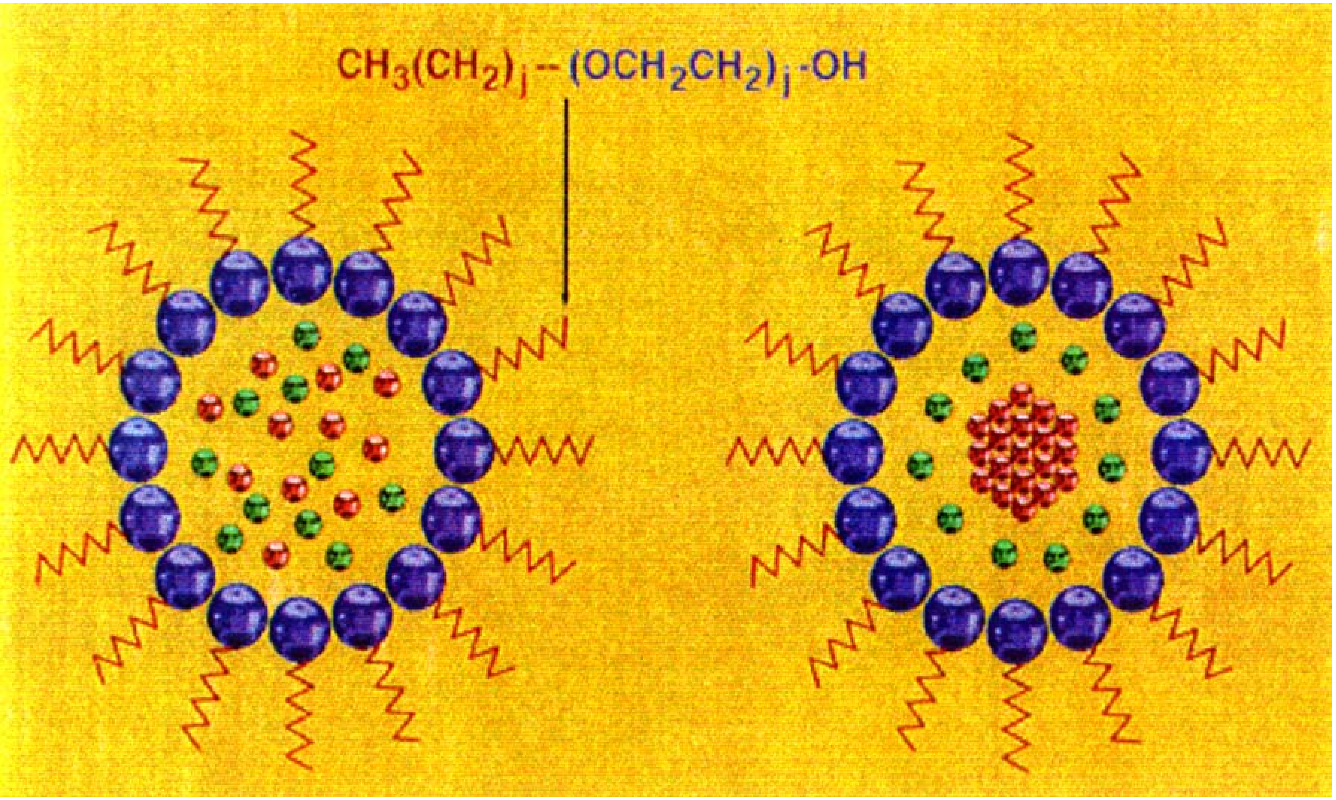
MoS_2, Like TiO_2 Has Exceptional Photostability-



- Kinetic stability occurs because both valence and conduction bands are localized on the metal, so carrier excitation doesn't weaken any chemical bonds

MoS_2 synthesis, purification, and characterization-

Synthesis in Inverse Micelle System

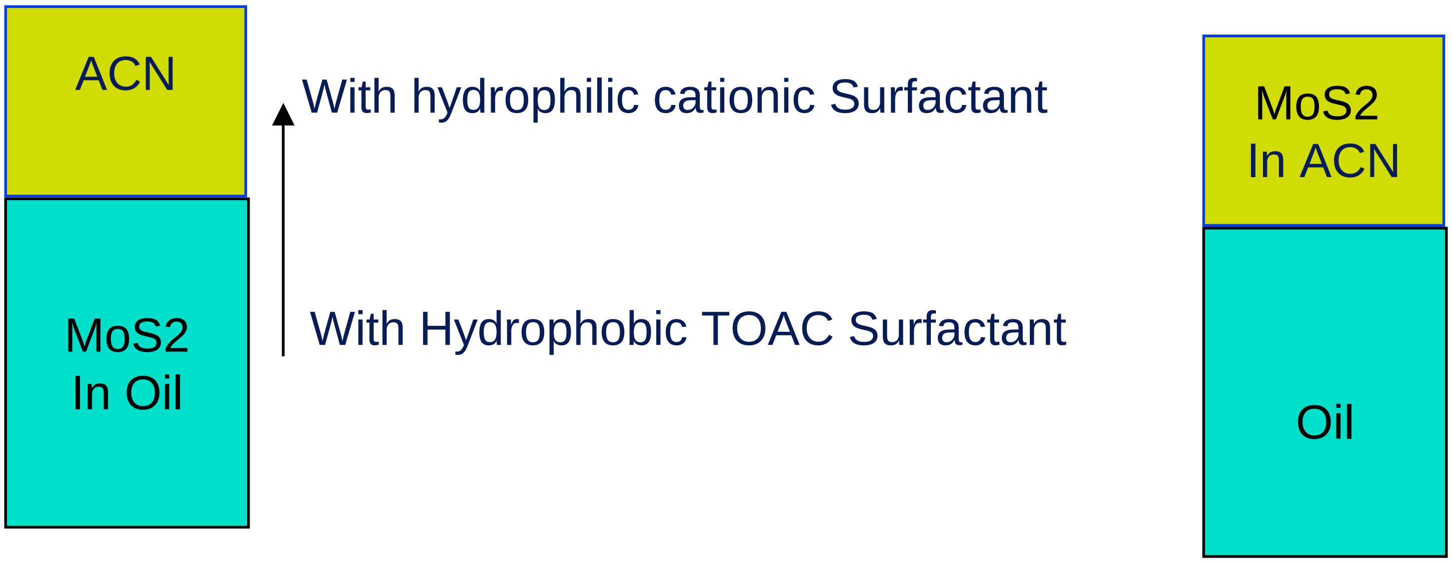


$$Mo^{4+} + 2S^{2-} = MoS_2$$

Mo Source: $MoCl_4$, S Source: H_2S, Oil: Octane

Typical Surfactant: Tri-ocytlmethylammonium Chloride (TOAC)

Purification by extraction into Acetonitrile (ACN)

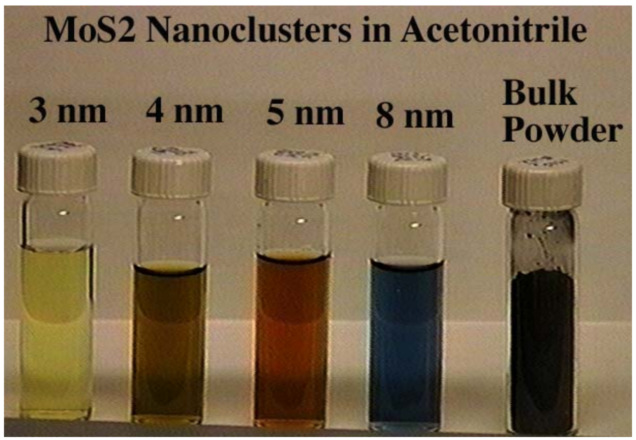


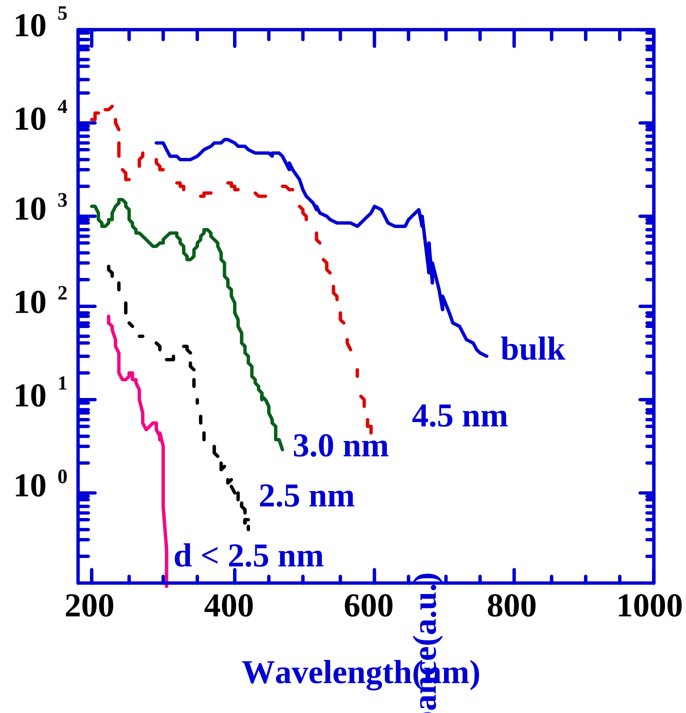
1) Liquid Chromatography shows the MoS_2 clusters have a net charge.

2) Samples diluted into water are dialized to remove unwanted ions like SO_4^{-2}

3) Analysis by XRF gives the final [Mo] and [Mo]:[S]~ 1 : 2.4 for D=3 nm.

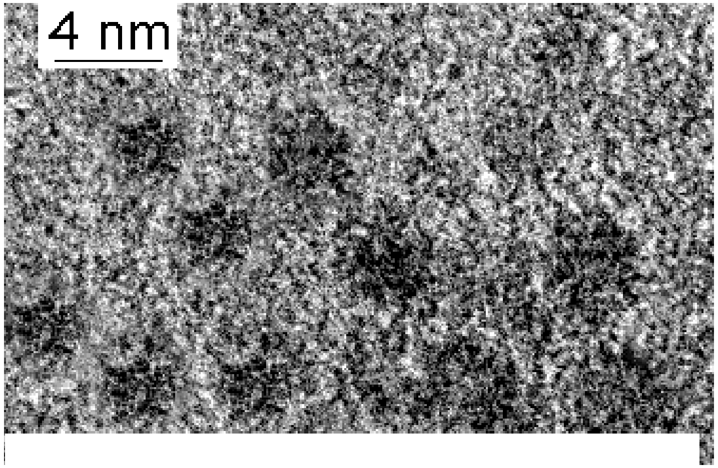
Quantum Size Effects influence the optical and electronic properties of the resulting solutions-

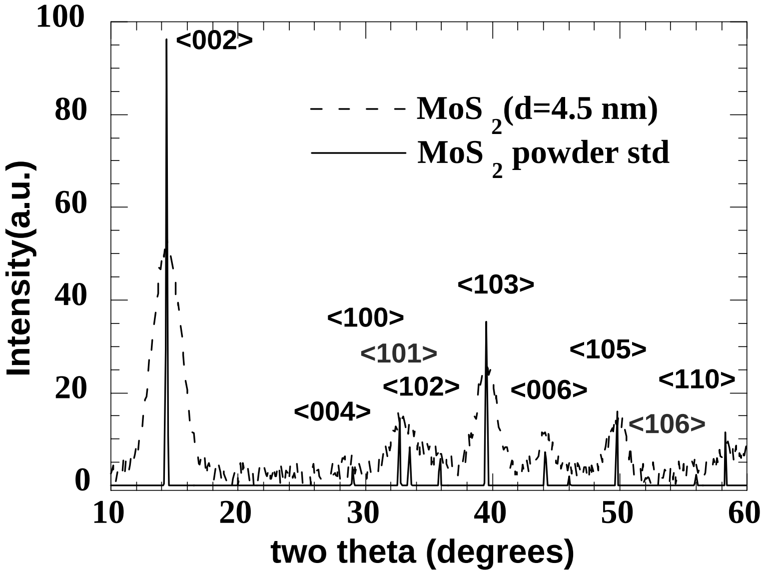


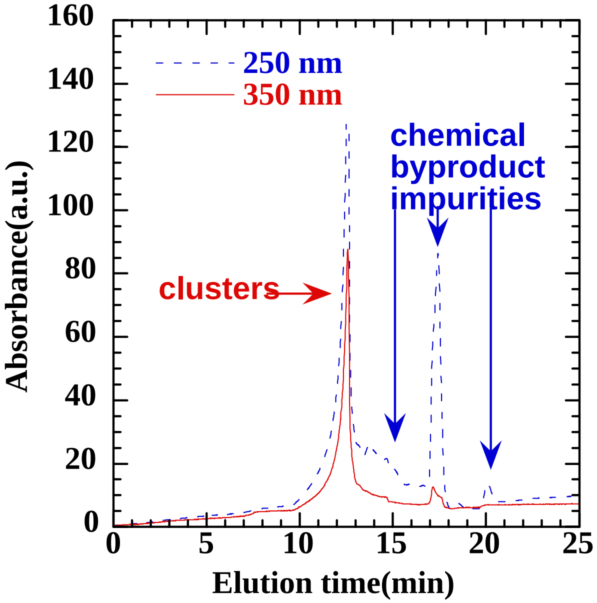


- By adjusting the size alone, the conductance and valence band energy levels can be shifted allowing new types of photocatalytic behavior to occur

Structural/Size Characterization-



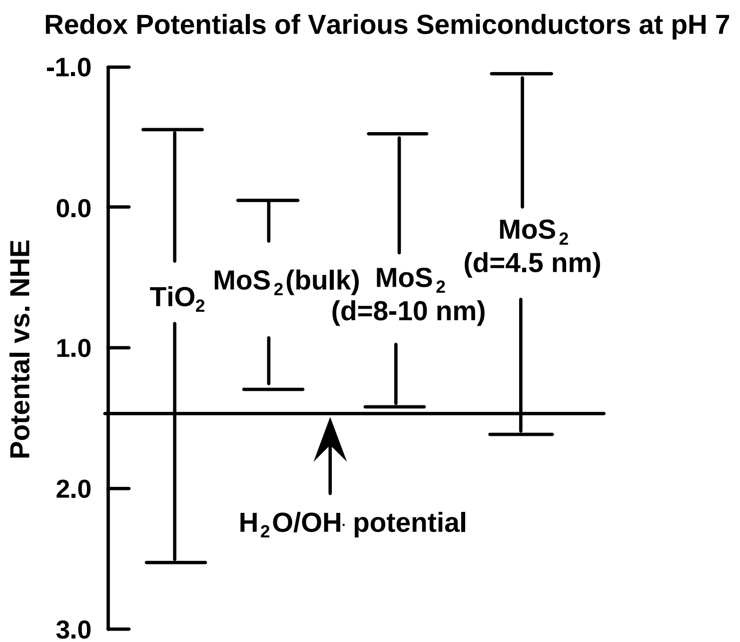


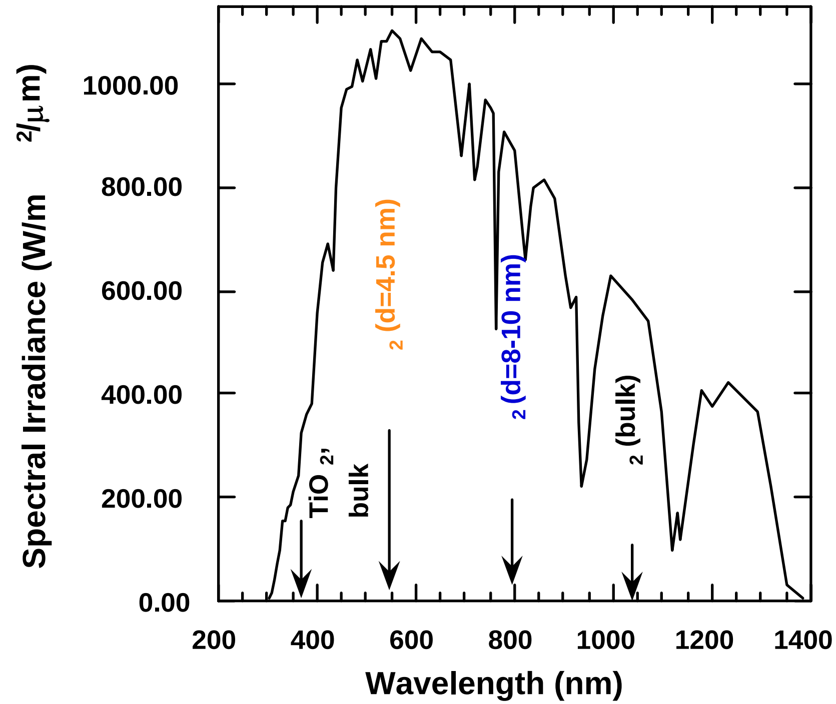


Chromatogram of clusters
Linewidth(polydispersity) comparable to chemical impurities

tsnl

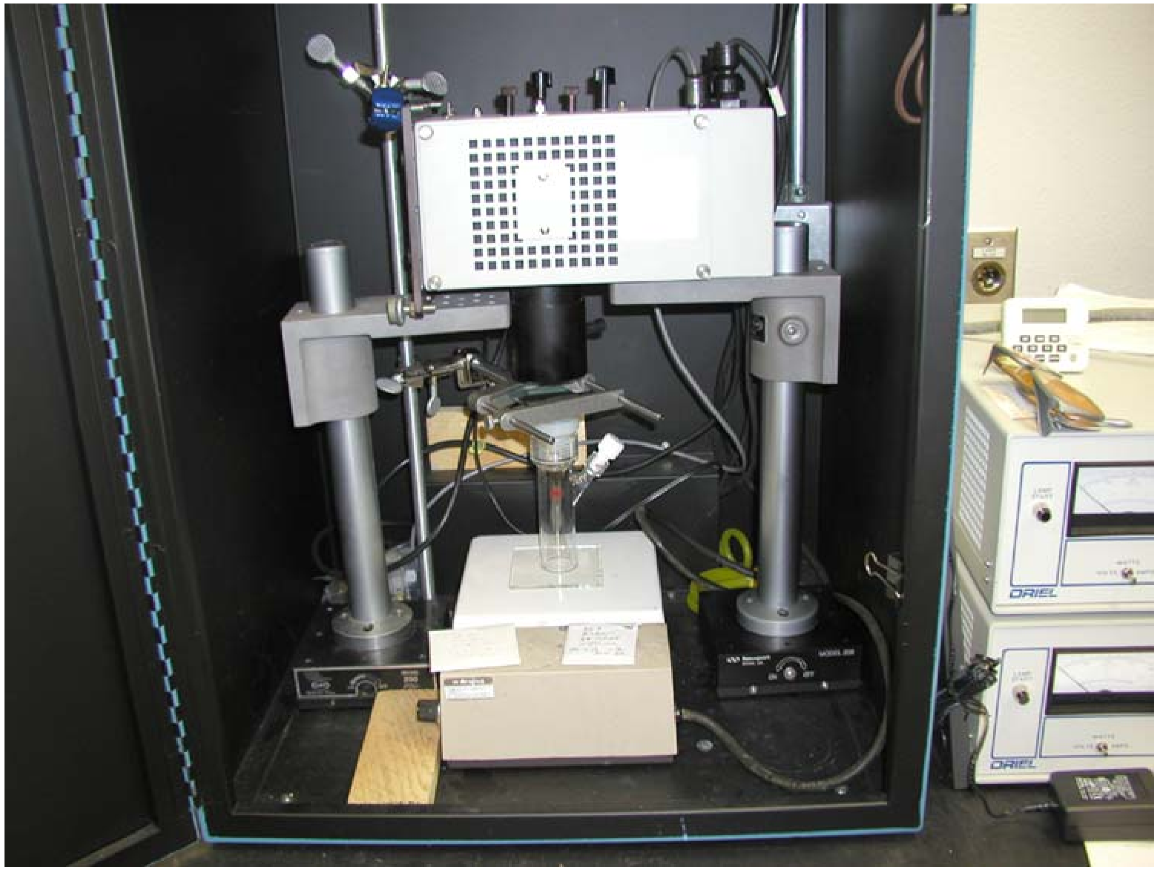
Light Absorbance and Redox Potentials-





- Greater light absorbance reduces the ability to oxidize a given organic.
- Mixtures of Nanoclusters will likely optimize the photooxidation process.

Photochemical Reactor-



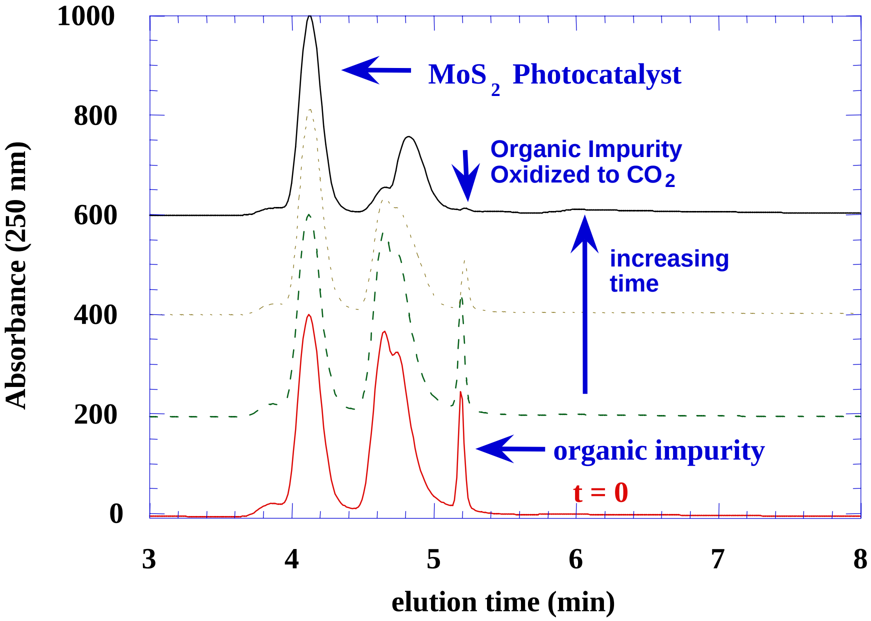
- 400 W Xe arc lamp with long pass filters.
- Cylindrical reactor with sampling port and overhead illumination.

Liquid Chromatography is Used to Follow the Kinetics of Photo-Redox Reactions-

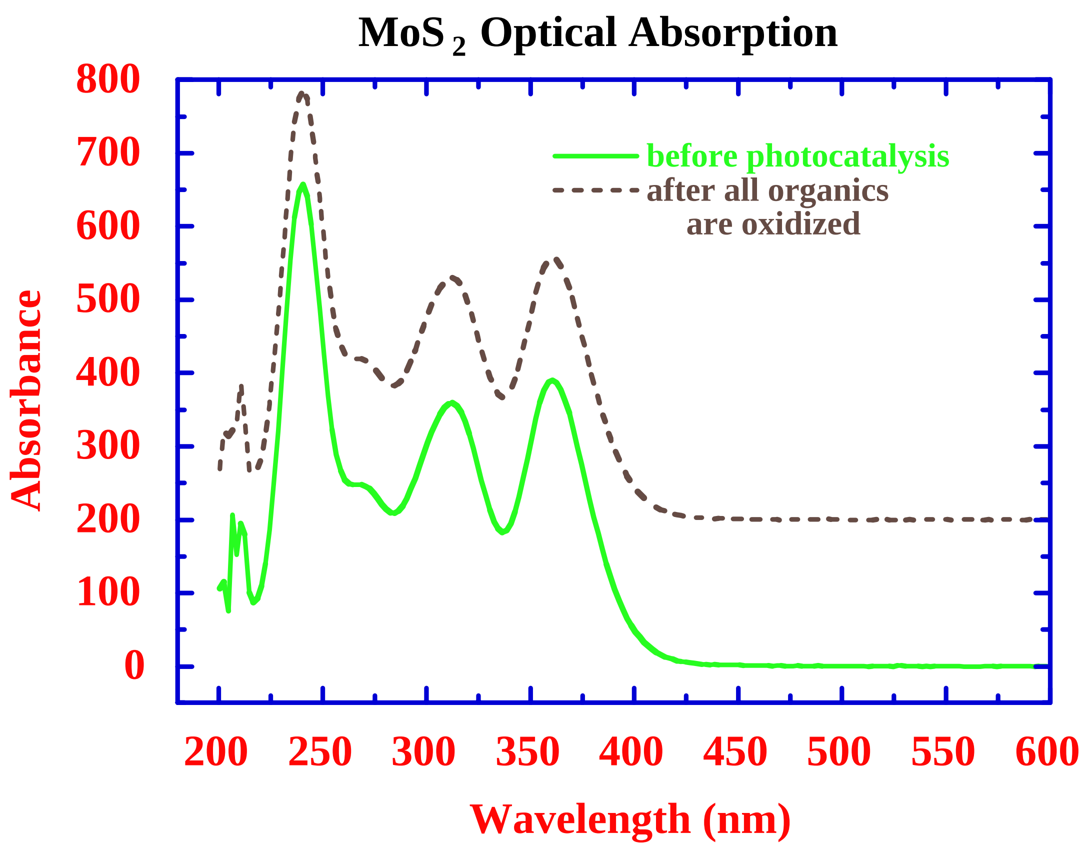
Basic Concept -

- Chemicals (and dispersed nanoclusters) travel through a porous medium which separates them and they elute at various times.
- The amount of chemical in each elution peak is measured using an absorbance or fluorescence detector and compared to known amounts of the same chemical.
- Intermediate break-down products are also identified.
- The size of the elution peak at a chosen absorbance wavelength gives the amount of each chemical.
- The stability of the nanosize photocatalyst can be determined from changes in the complete absorbance spectrum at its elution peak.

Example - Destruction of an Alkyl Chloride Organic Impurity using dispersed nanosize (D = 3 nm) MoS_2.

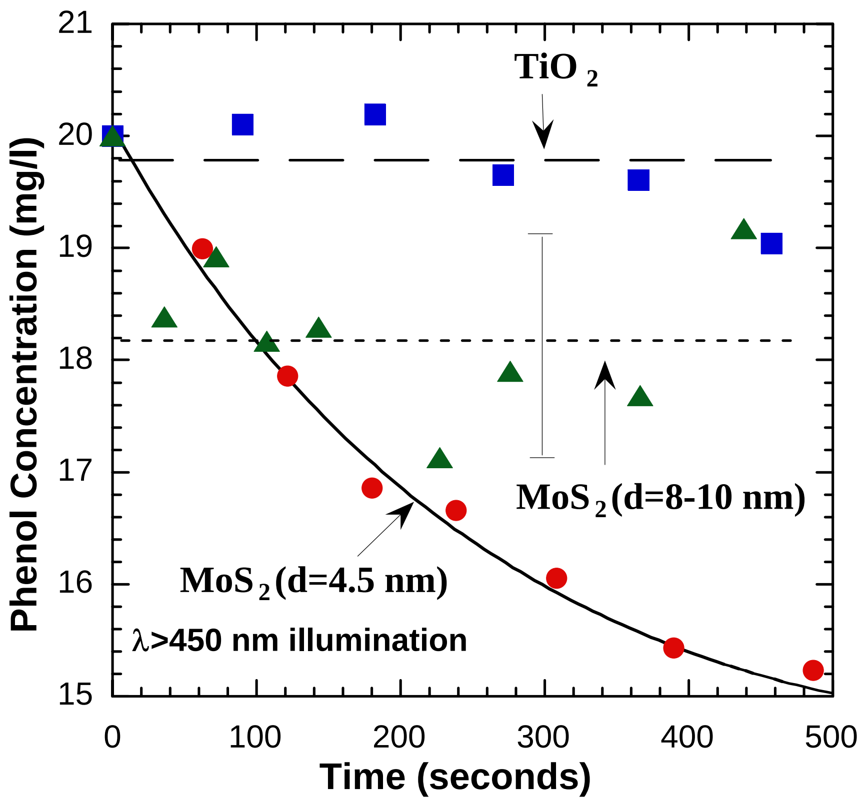


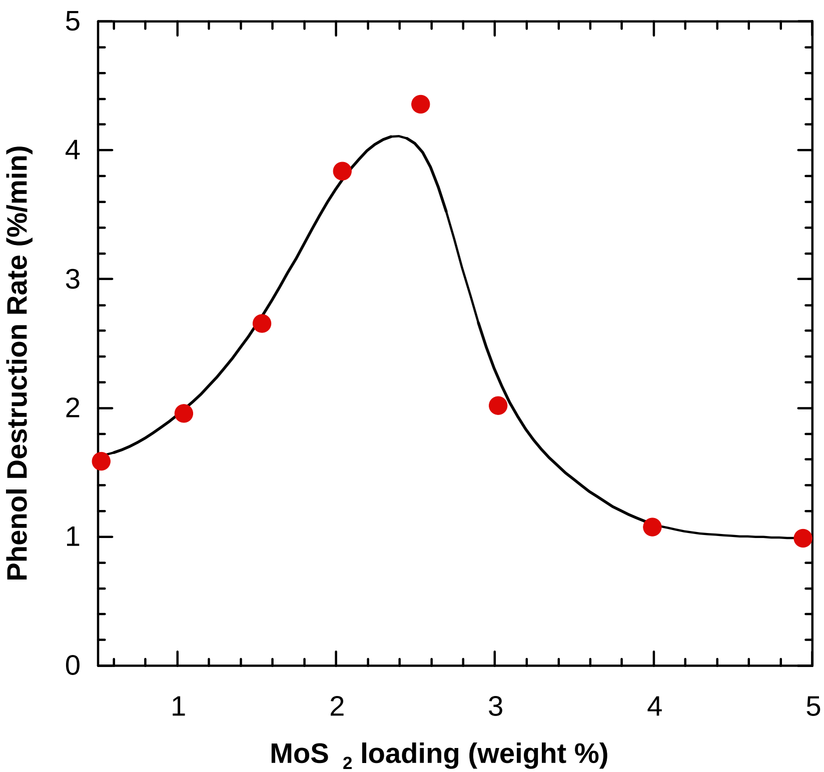
Optical Absorbance of Nanocluster Catalyst is Unchanged-



- *No reduction in optical absorbance, nanocluster concentration, or photocatalytic activity were observed*

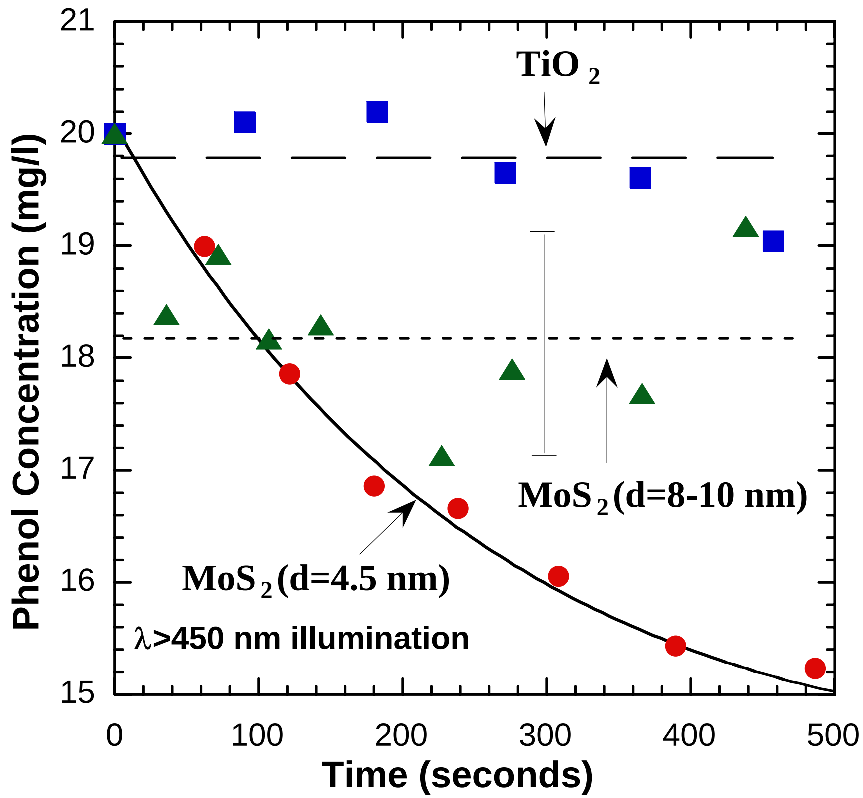
Photocatalysis of Phenol Using Nanosize MoS_2 Supported on TiO_2 Powder





- **Visible Light Absorbance by MoS_2.**
- **Carrier transfer between MoS_2 and TiO_2 slurry particles decreases recombination rate and increases photooxidation rate of organic.**

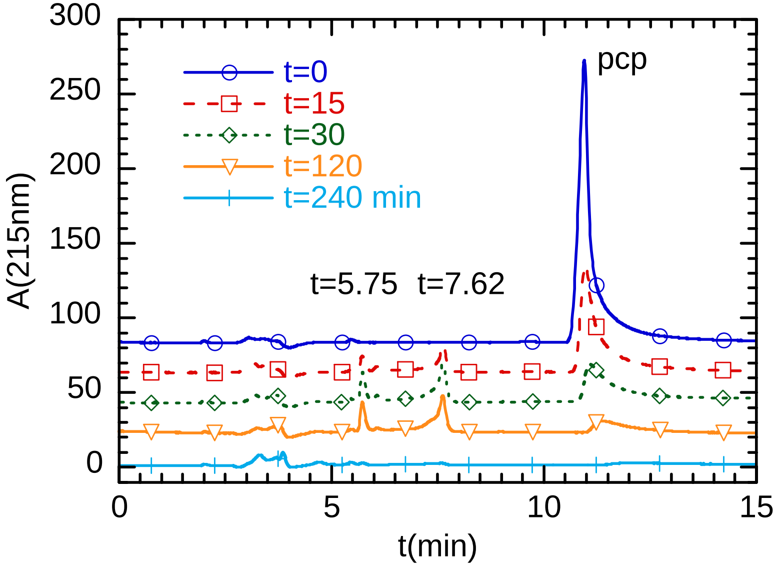
Photocatalysis of Phenol Using Nanosize MoS_2 Supported on TiO_2 Powder



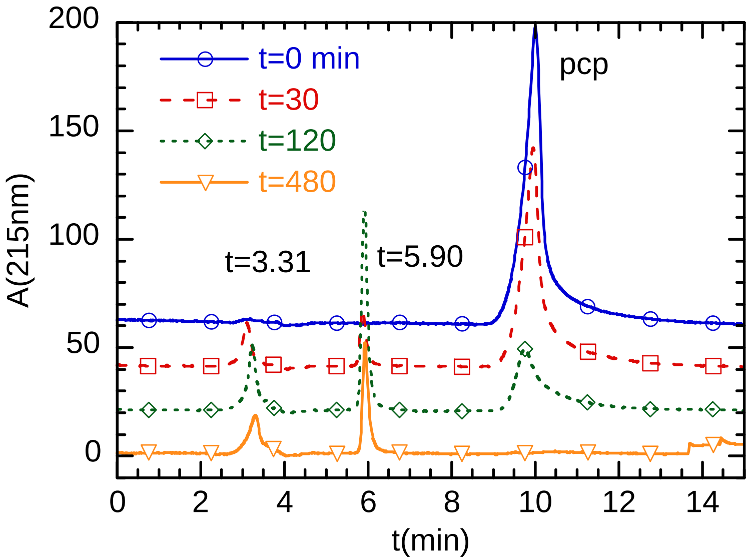
- **Visible (λ>450 nm)Light Absorbance by MoS_2 shows exponential photo-oxidation kinetics.**
- **A strong size dependence of photo-oxidation rate is observed.**

Pentachlorophenol (PCP) Photocatalysis Studies-

PCP UV Photooxidation Results using TiO_2 (Degussa)



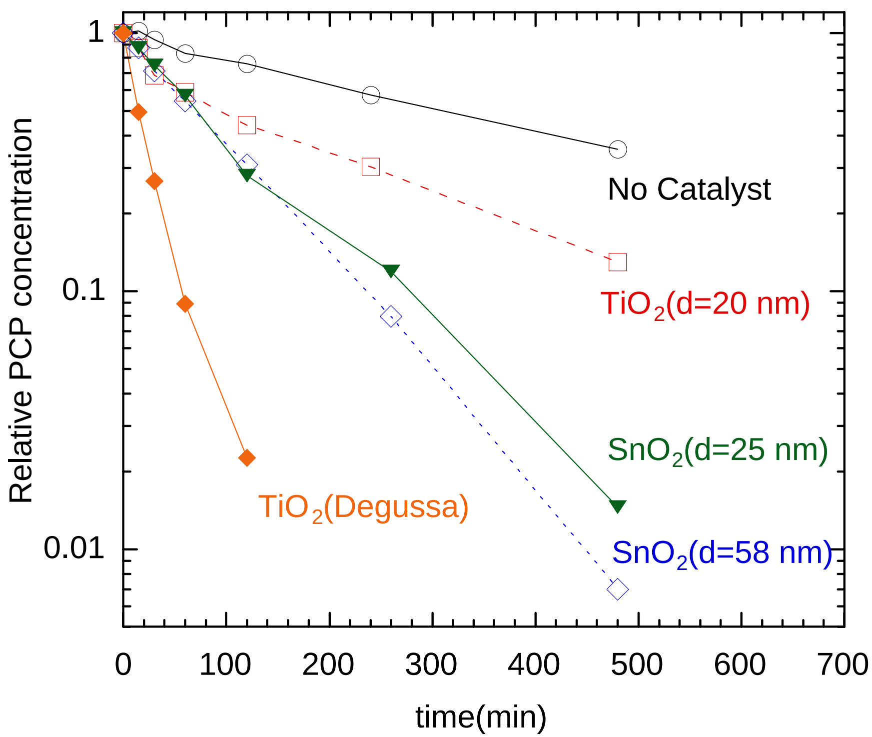
UV Photooxidaton using D=25 nm, SnO_2 Clusters



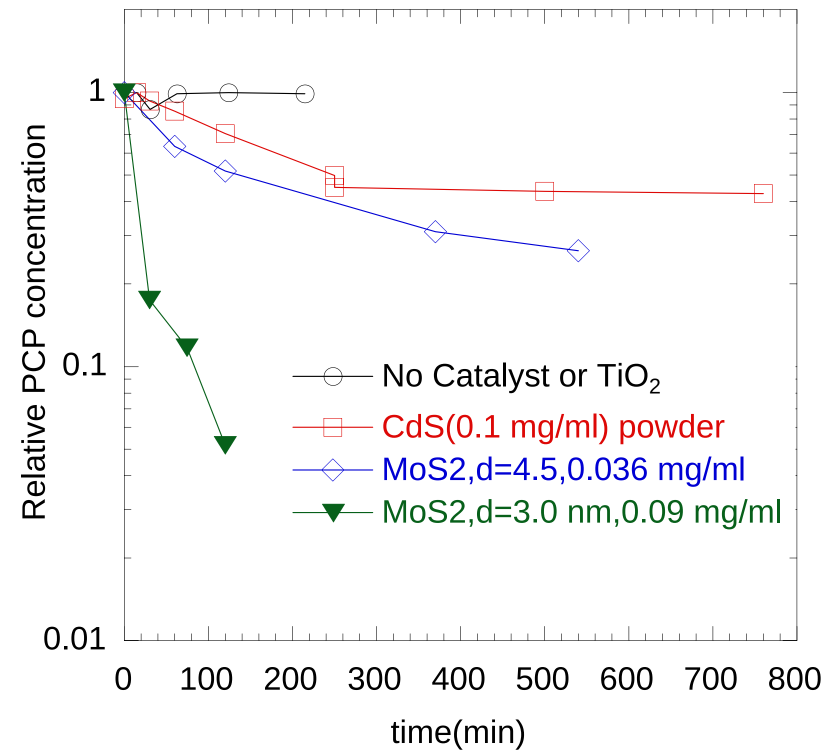
- *Intermediate Photooxidation Products Depend on Catalyst Material*

PCP Photooxidation Results(Summary)

PCP UV Photooxidation Results



Visible Light Photooxidation Results



- CO_2 measured at end of reaction confirms total photooxidation of PCP.

Conclusions

- **Photo-oxidation of an alkyl chloride by nanosize MoS_2 shows a strong size dependence and occurs with weak visible illumination.**

- **HPLC analysis demonstrates that no changes occur in the quantity or absorbance properties of nanosize MoS_2 during the photooxidation of this alkyl chloride.**

- **Both nanosize SnO_2 and MoS_2 show a strong size-dependent photocatalytic activity.**

- **Nanosize MoS_2 can be an effective photocatalyst for PCP photo-oxidation even with only visible (λ>400 nm) light.**

Future Directions

- Improve nanocluster/support interactions by heat treatments after deposition of nanoclusters to improve photocatalysis kinetics.

- Examine nanocluster systems with mixed sizes (bandedges and potentials) to optimize solar absorbance while still allowing a sufficient driving force for the photooxidation process.

- Examine the photooxidation of long-lived organics such as pesticides, and polycyclic aromatics using nanosize MoS_2 to determine reaction kinetics and final breakdown products.

- Investigate alternative, highly stable nanocluster catalysts (RuS_2, WS_2) and compare with MoS_2.

- Investigate other small molecule photoredox reactions (e.g. H_2O or H_2S reduction.