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

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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.

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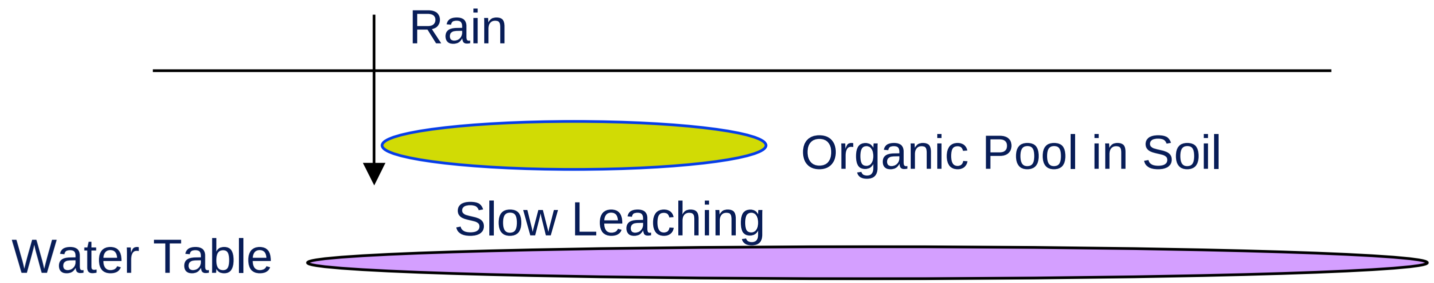
Typical Scenario-Dense Non-Aqueous Solvent Pools



- 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

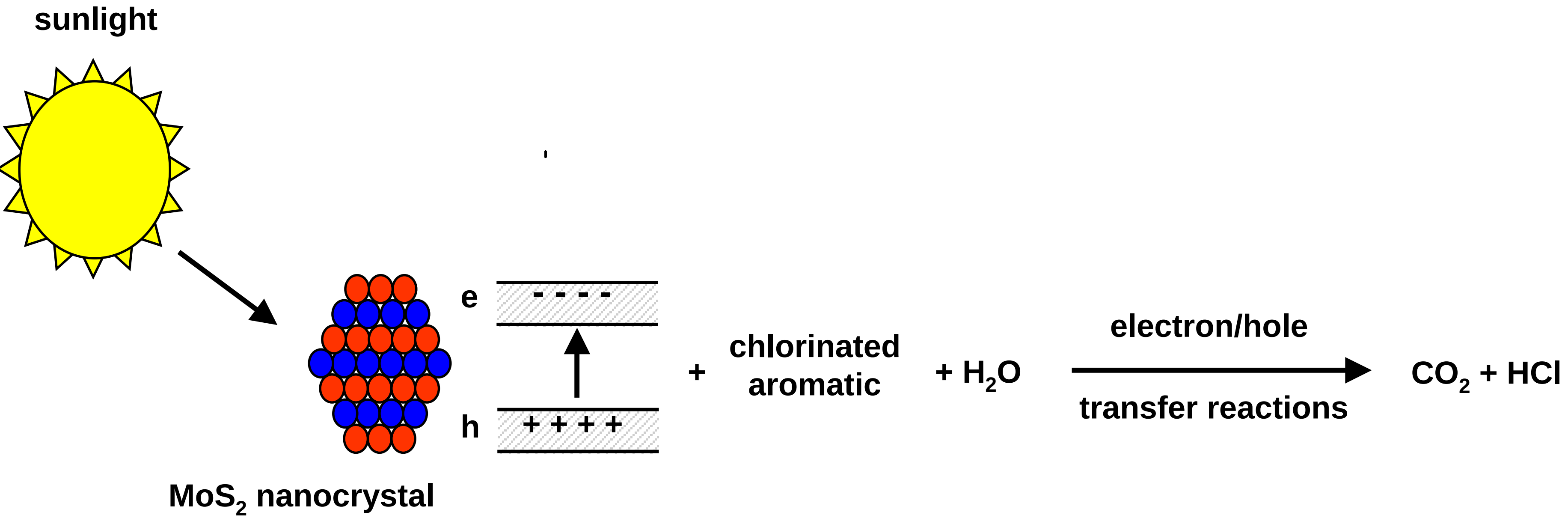
3)Deep UV Photooxidation of the Organics

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)*

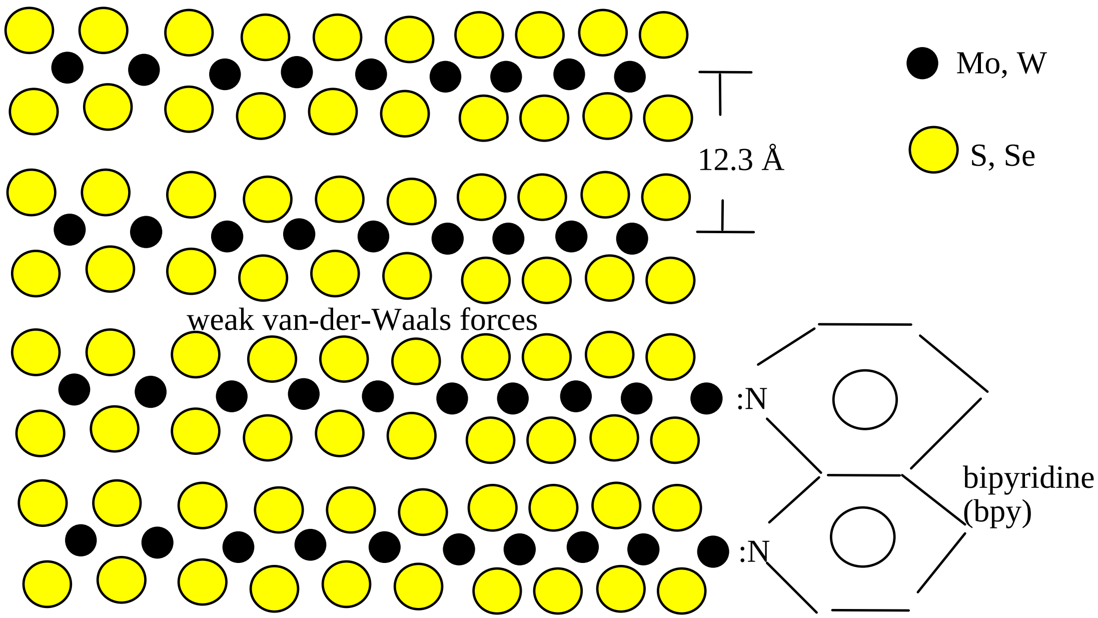
Advantanges of this Approach-

- 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 -

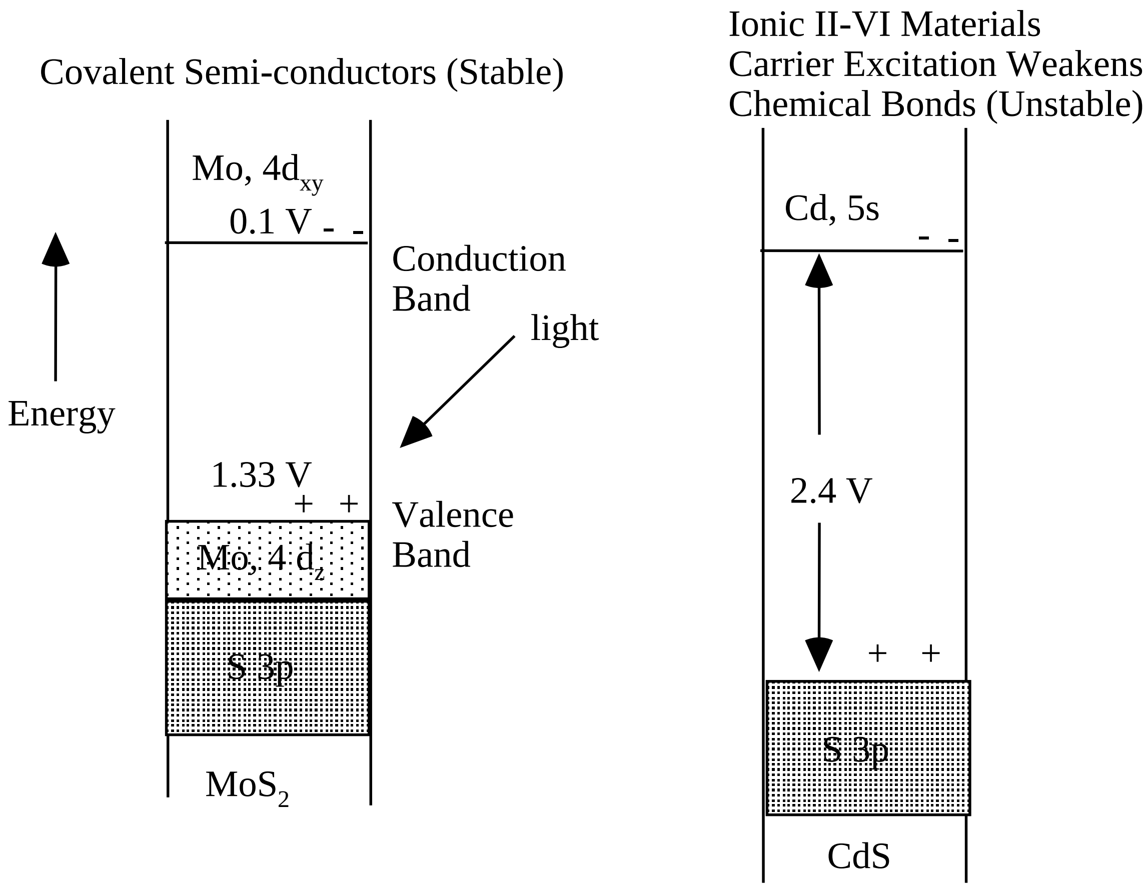
1) Efficient conversion of sunlight to electron-hole pairs.
2) Surface trapping of electrons and holes before recombination.
3) Catalyst photostability.
4) Inexpensive, chemically-stable, environmentally benign materials.

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

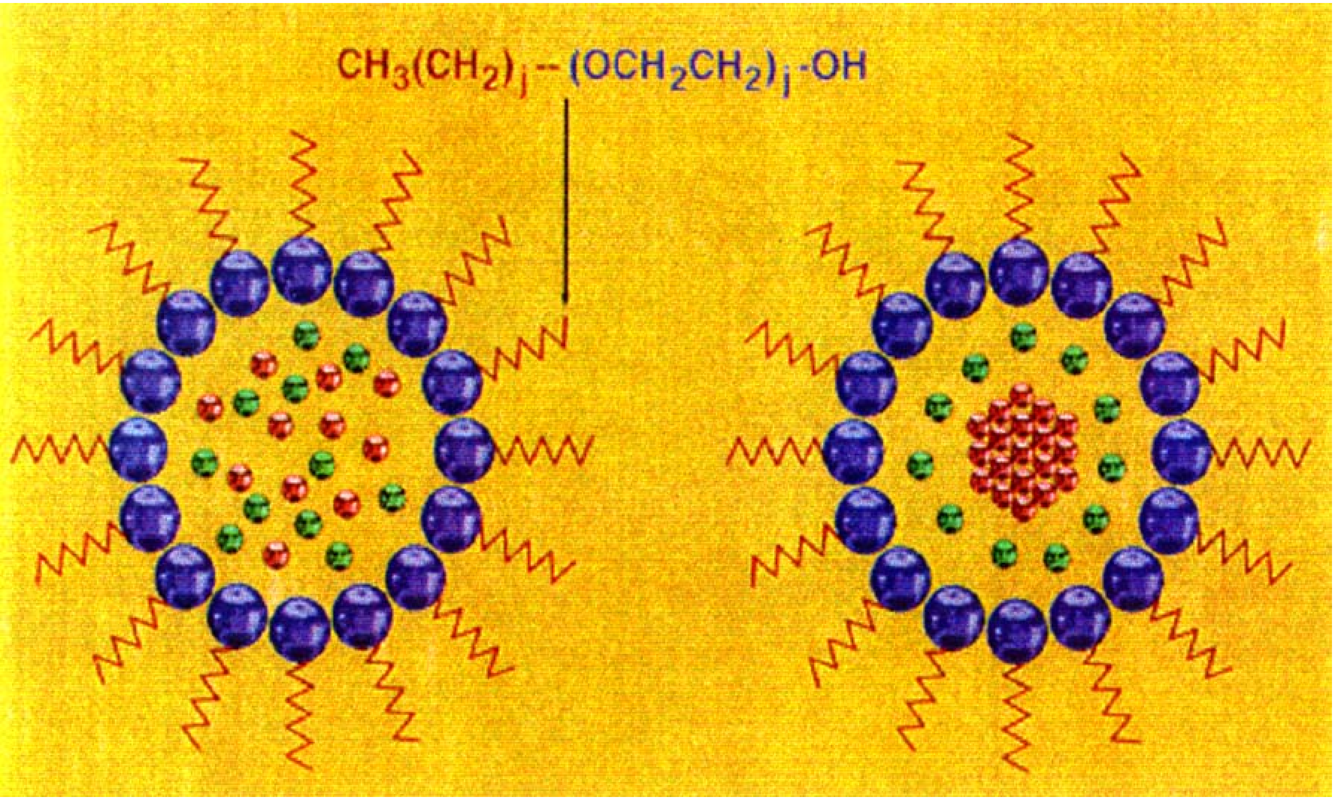
MoS_2, Like TiO_2 Has Exceptional Photostability-



- 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

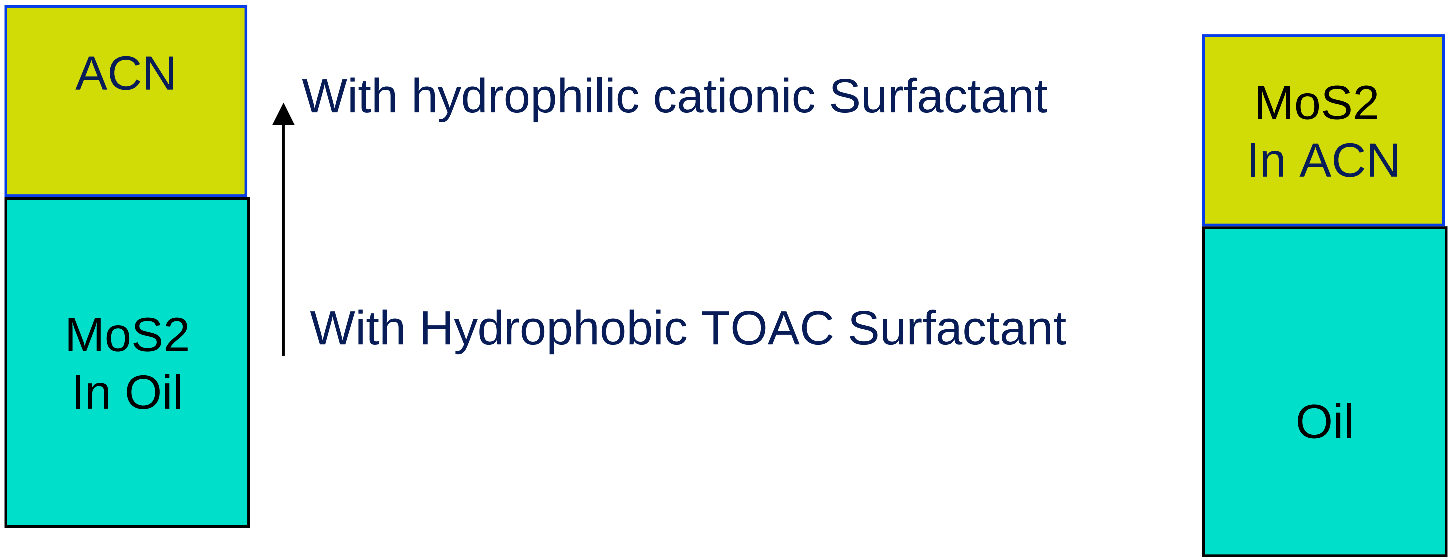


$$Mo^{4+} + 2S^{2-} = MoS_2$$

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

Typical Surfactant: Tri-ocytlmethylammonium Chloride (TOAC)

Purification by extraction into Acetonitrile (ACN)

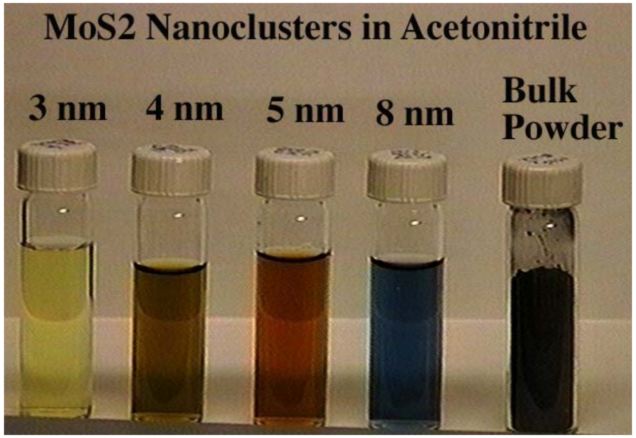


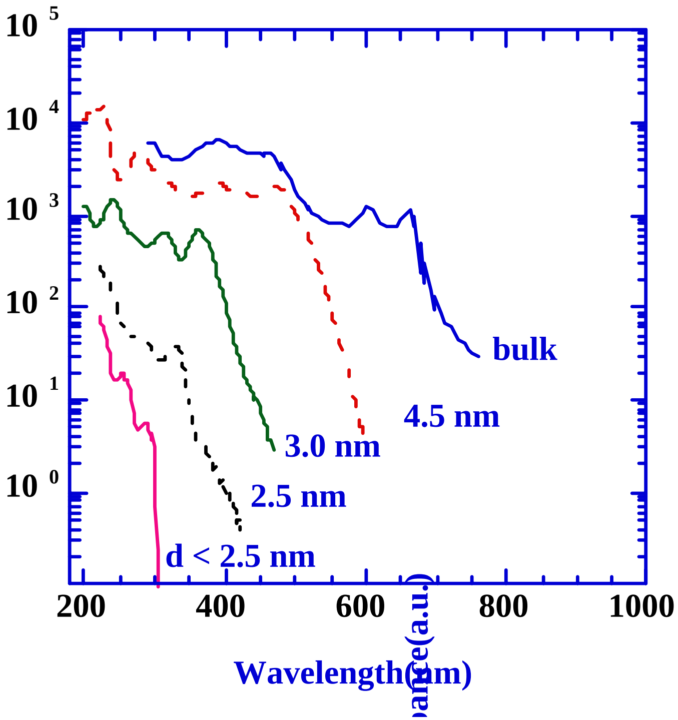
1) Liquid Chromatography shows the MoS_2 clusters have a net charge.

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.

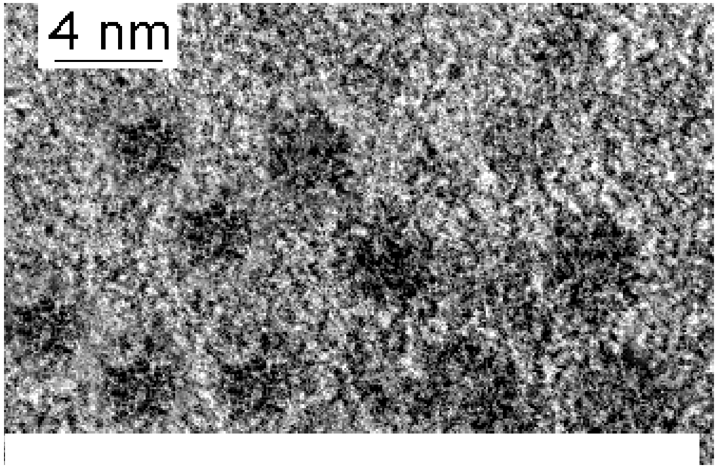
Quantum Size Effects influence the optical and electronic properties of the resulting solutions-

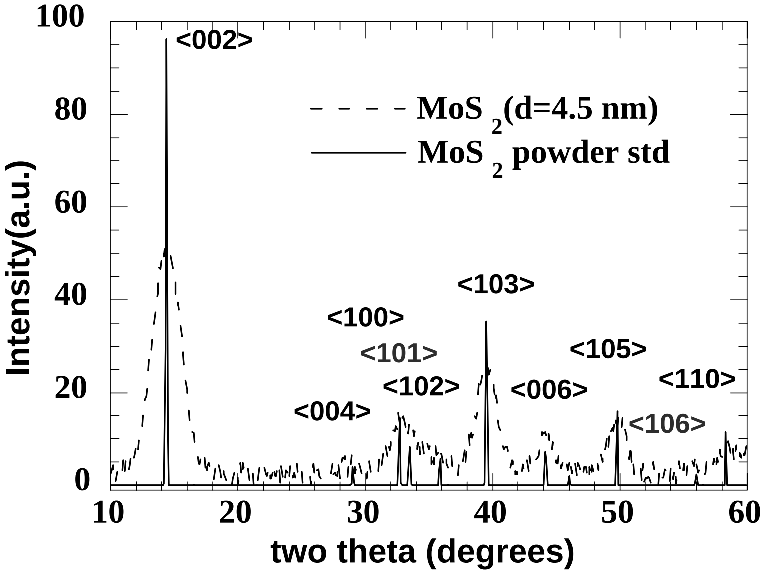


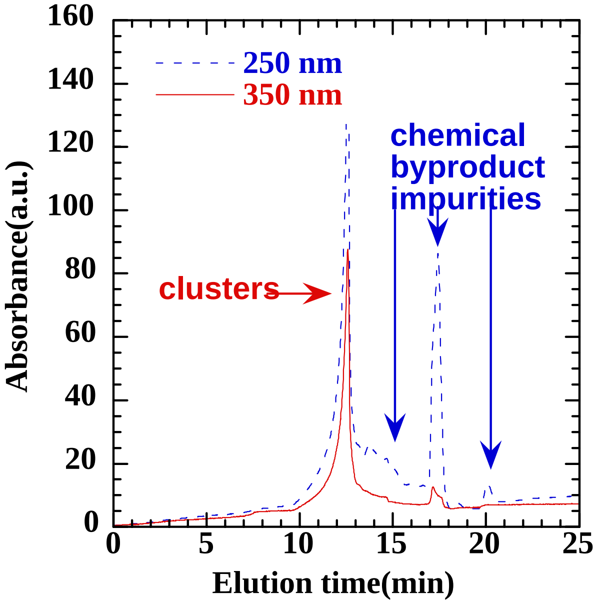


- By adjusting the size alone, the conductance and valence band energy levels can be shifted allowing new types of photocatalytic behavior to occur

Structural/Size Characterization-

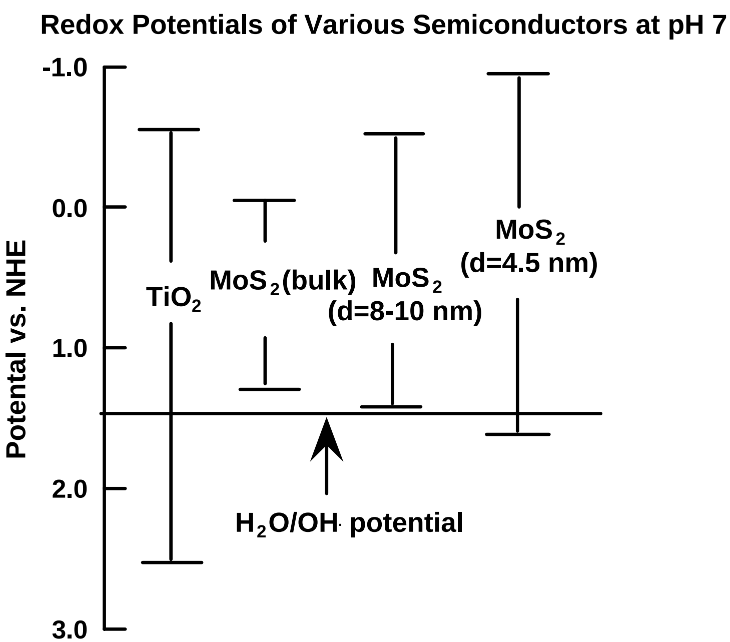


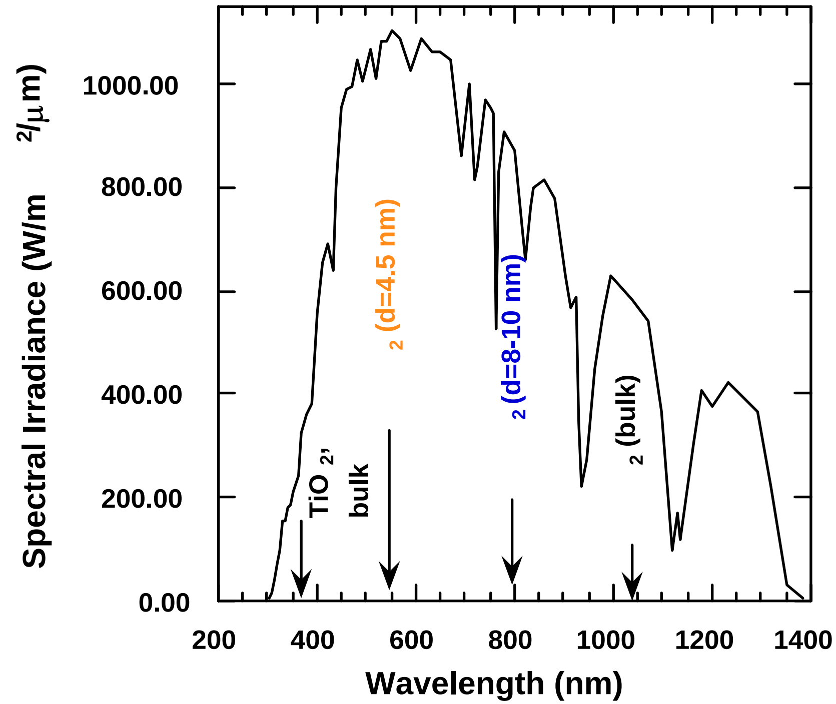




Chromatogram of clusters
Linewidth(polydispersity) comparable to chemical impurities

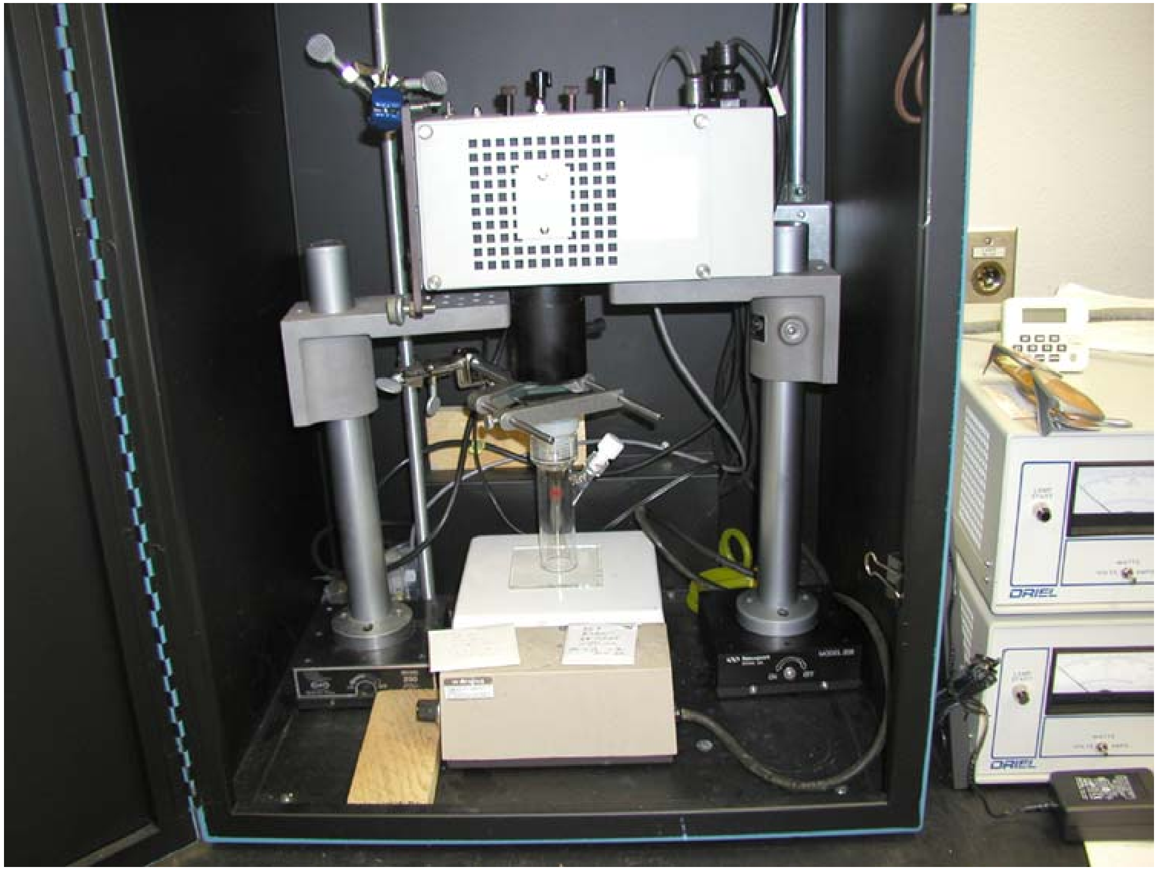
Light Absorbance and Redox Potentials-





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

Photochemical Reactor-



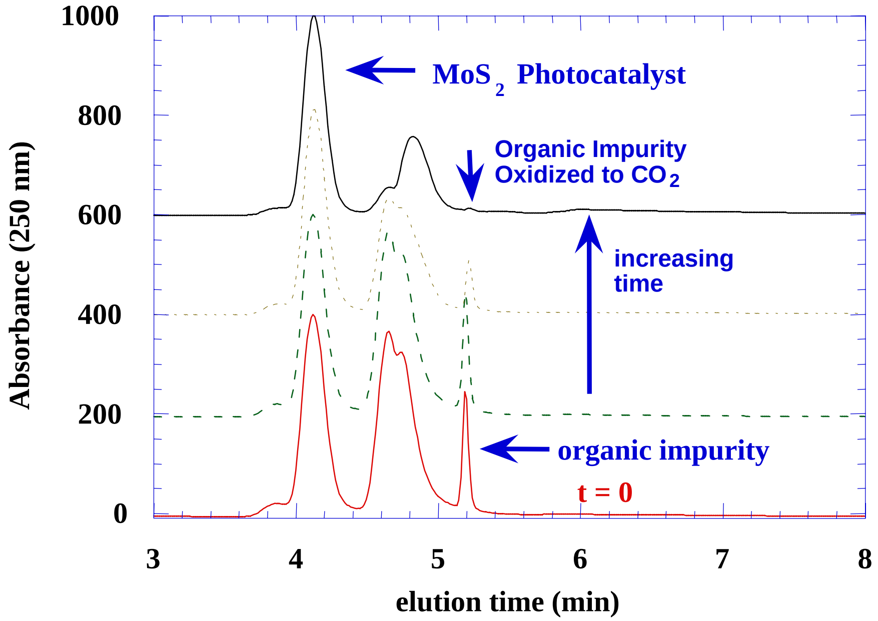
- 400 W Xe arc lamp with long pass filters.
- Cylindrical reactor with sampling port and overhead illumination.

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

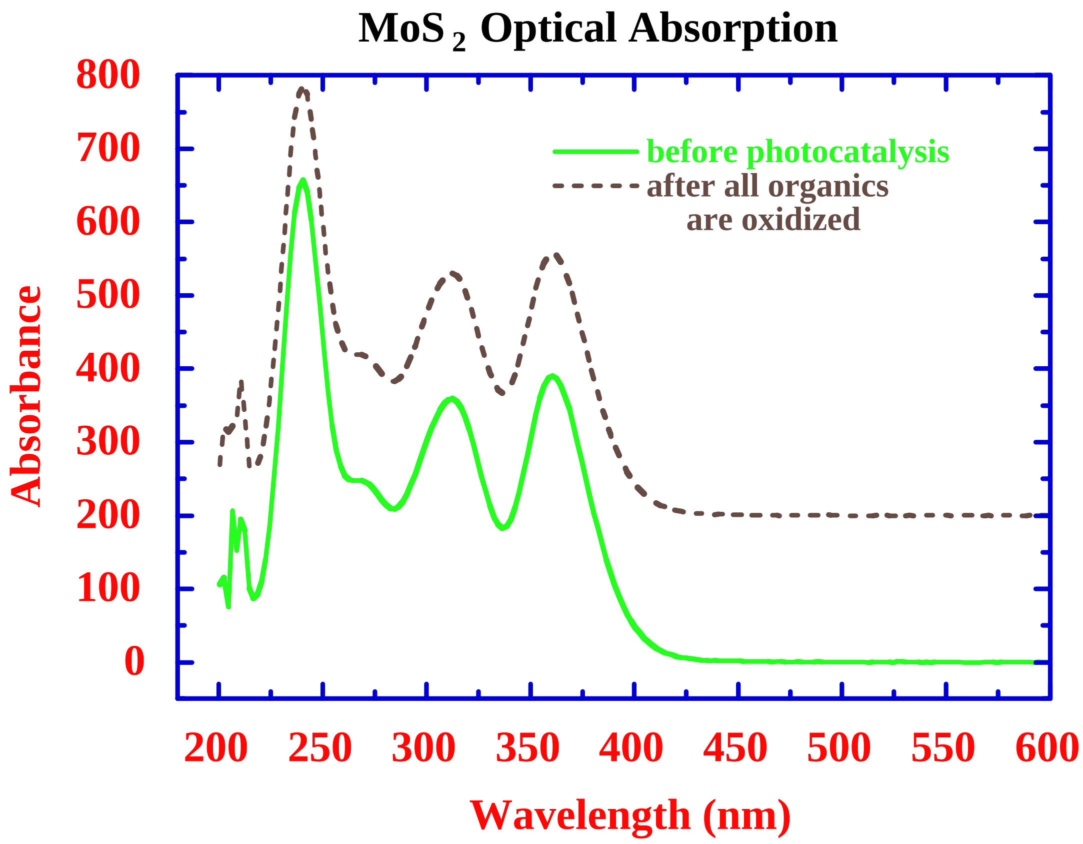
Basic Concept -

- 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.

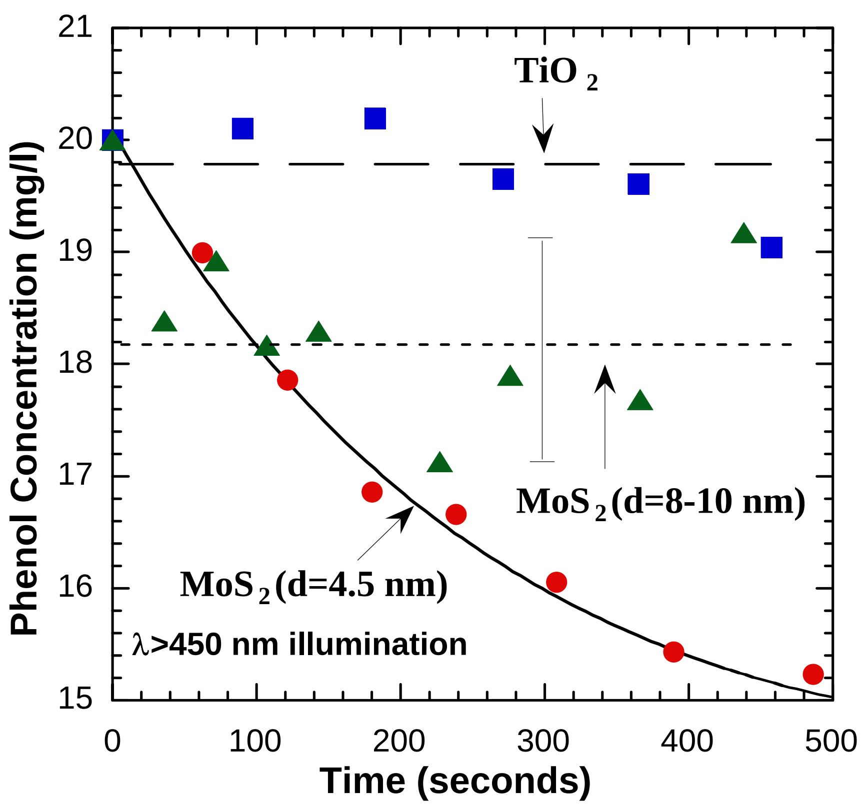


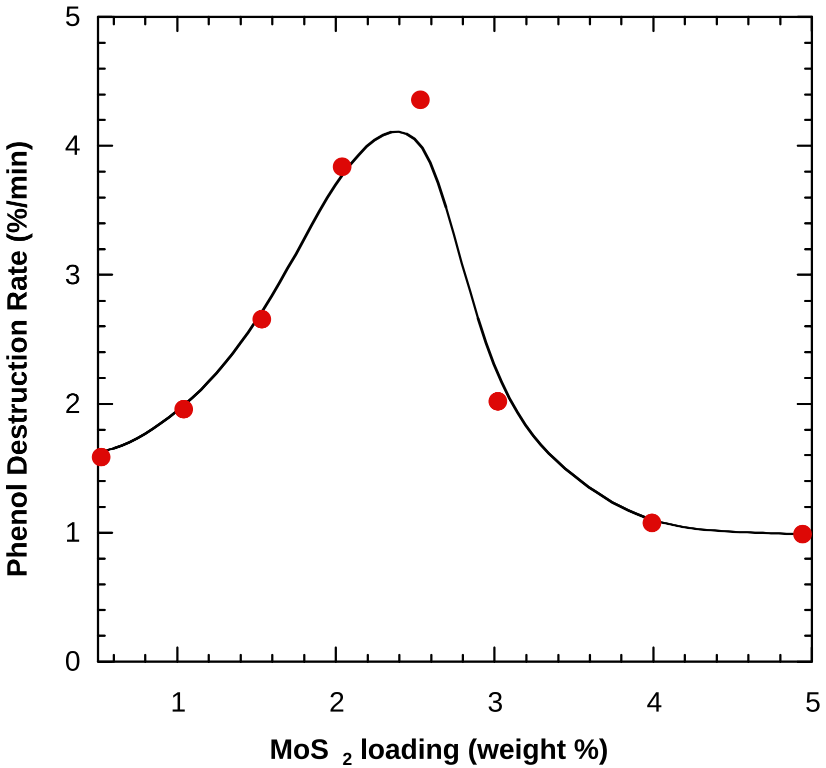
Optical Absorbance of Nanocluster Catalyst is Unchanged-



- *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.**

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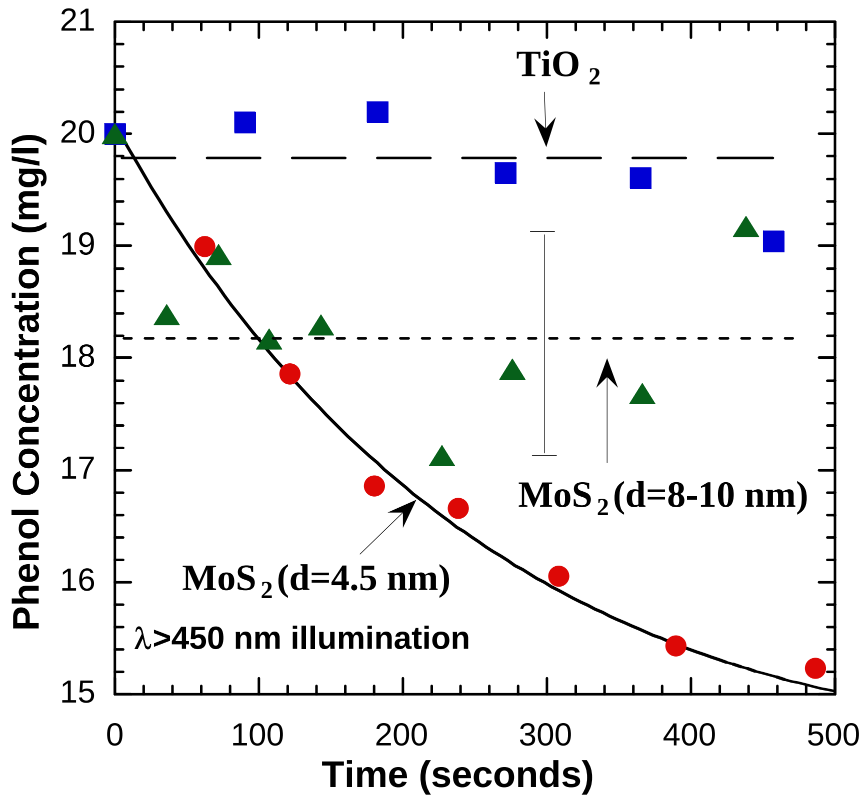
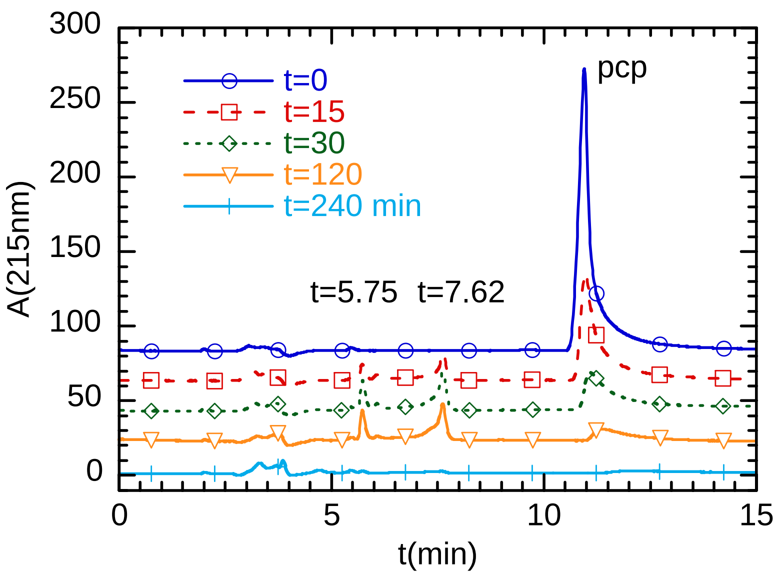


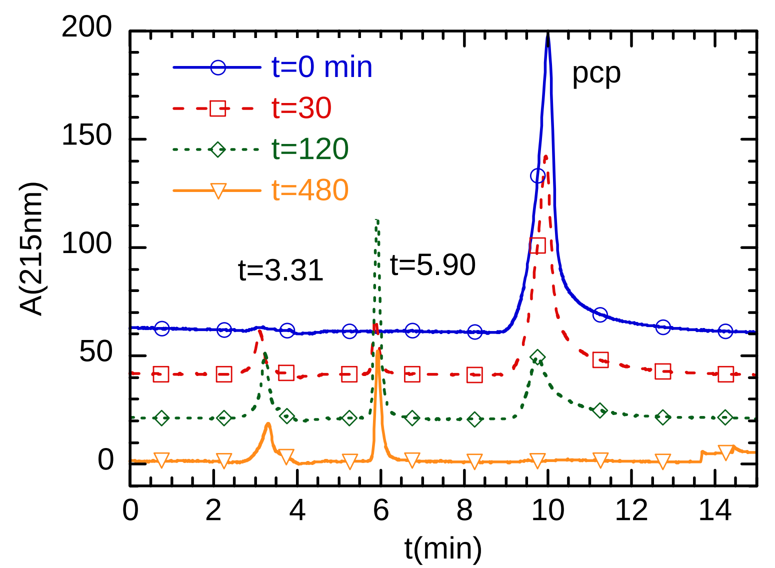
- **Visible (λ>450 nm)Light Absorbance by MoS_2 shows exponential photo-oxidation kinetics.**
- **A strong size dependence of photo-oxidation rate is observed.**

Pentachlorophenol (PCP) Photocatalysis Studies-

PCP UV Photooxidation Results using TiO_2 (Degussa)



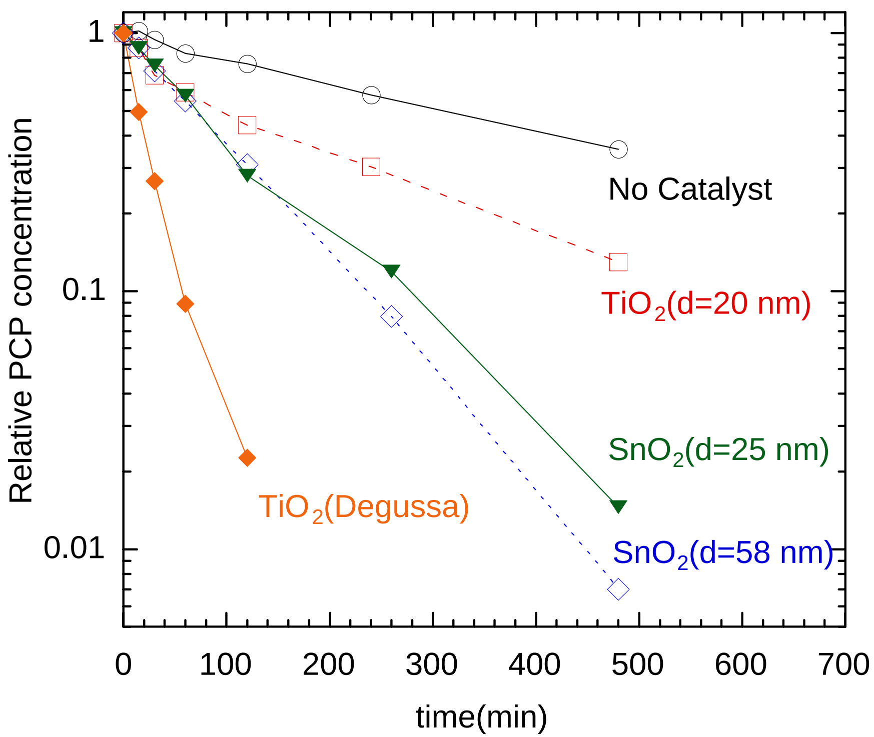
UV Photooxidaton using D=25 nm, SnO_2 Clusters



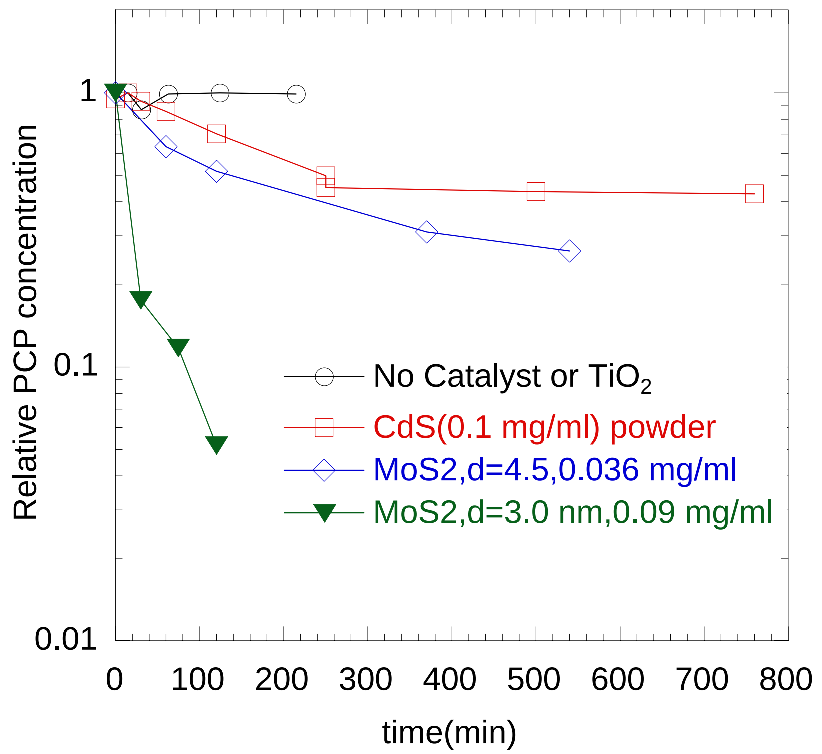
- *Intermediate Photooxidation Products Depend on Catalyst Material*

PCP Photooxidation Results(Summary)

PCP UV Photooxidation Results



Visible Light Photooxidation Results



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

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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.