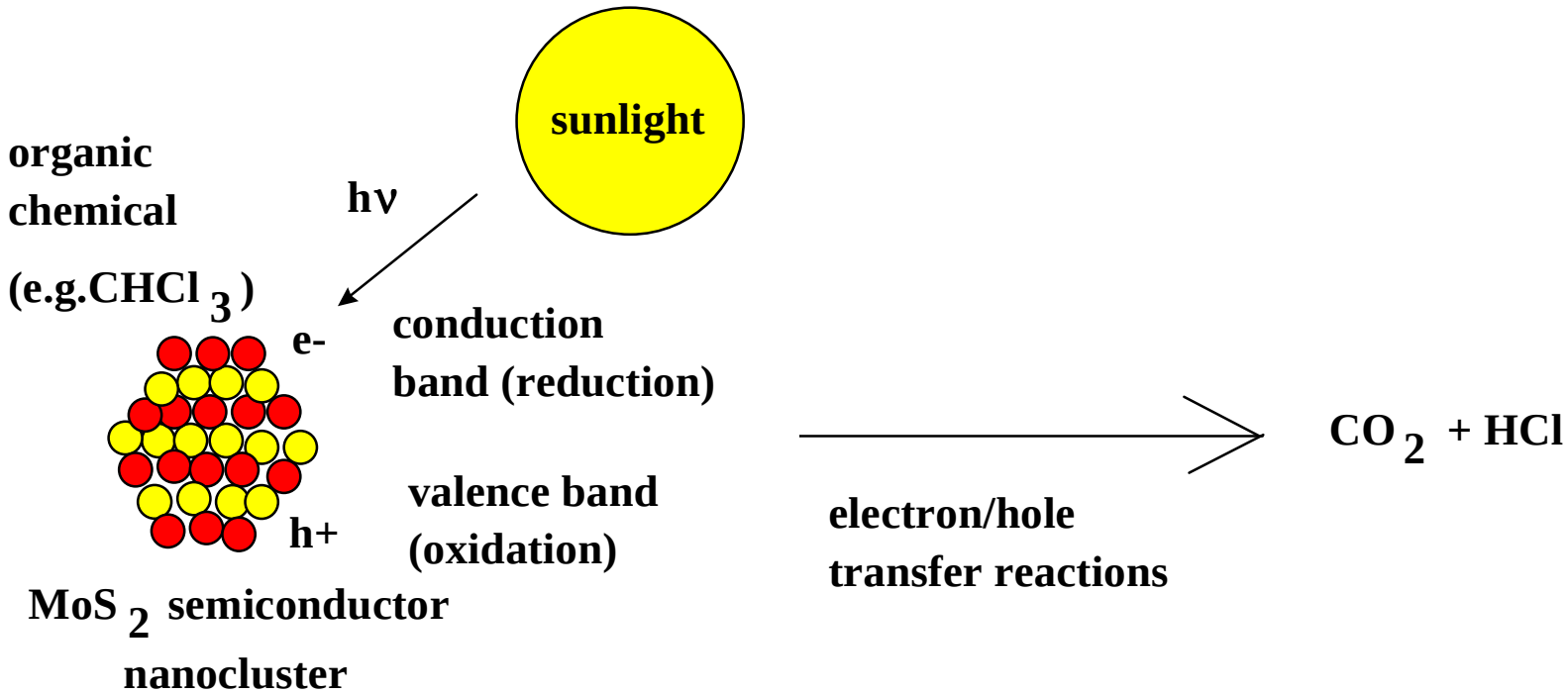
Approach

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



Advantages of 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 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.

Research Issues

Our project addresses five important issues in achieving economically viable solar detoxification:

1) the efficient conversion of sunlight to electron-hole pairs
2) the surface trapping of electrons and holes before recombination
3) photostability of the catalyst
4) short metal-metal bond distances in the lattice
5) the use of cheap, chemically-stable, environmentally benign materials

Program Highlights

- Demonstrated the photo-oxidation of an organic (alkyl chloride) using dispersed MoS_2 nanoclusters and low intensity visible light.
- Using liquid chromatography we showed that the MoS_2 nanoclusters were not altered chemically or photodegraded during this photodestruction process.
- Using time-resolved photoluminsence spectroscopy we showed that electron transfer rates from nanosize MoS_2 to an organic (bipyridine) were vastly accelerated as the nanoclusters were made smaller (larger bandgap).
- Based upon measured electron transfer rates we determined that polar solvents such as water accelerate the transfer kinetics. This means photo-redox reactions will proceed fastest in polar solvents-just as desired.
- Deposited nanosize MoS_2 onto bulk TiO_2 powder and demonstrated that facile destruction of phenol occurred using only visible light.
- Established the optimum loading of nanosize MoS_2 onto TiO_2 occurs near 2%, where the phenol oxidation rate is enhanced ~2-fold compared to TiO_2 alone.
- Demonstrated destruction of phenol and pentachlorophenol using both dispersed and supported nanosize MoS_2 and showed that the optimum bandedge absorbance is ~550 nm (size = 4.5 nm) for dispersed and ~700 nm (size = 8 nm) for supported nanoclusters.

Nanocluster Size Determines the Optical Absorption (Color)

Our Approach - Inverse Micellar Synthesis & Processing

Characterization Vital to Improvements in Photocatalytic Activity

Materials must be nanocrystallline

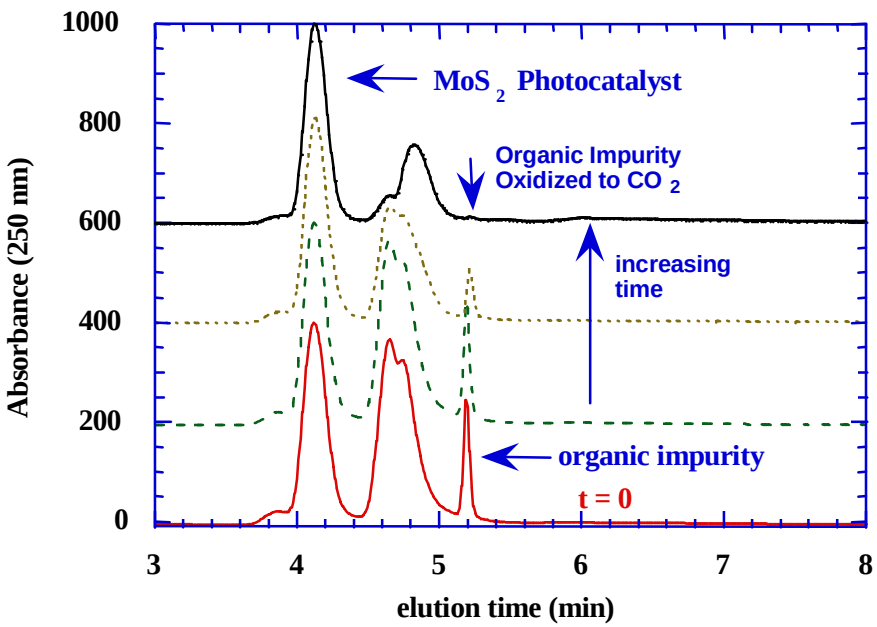
And reasonably monodisperse (so the optical/electronic properties are predictable)

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

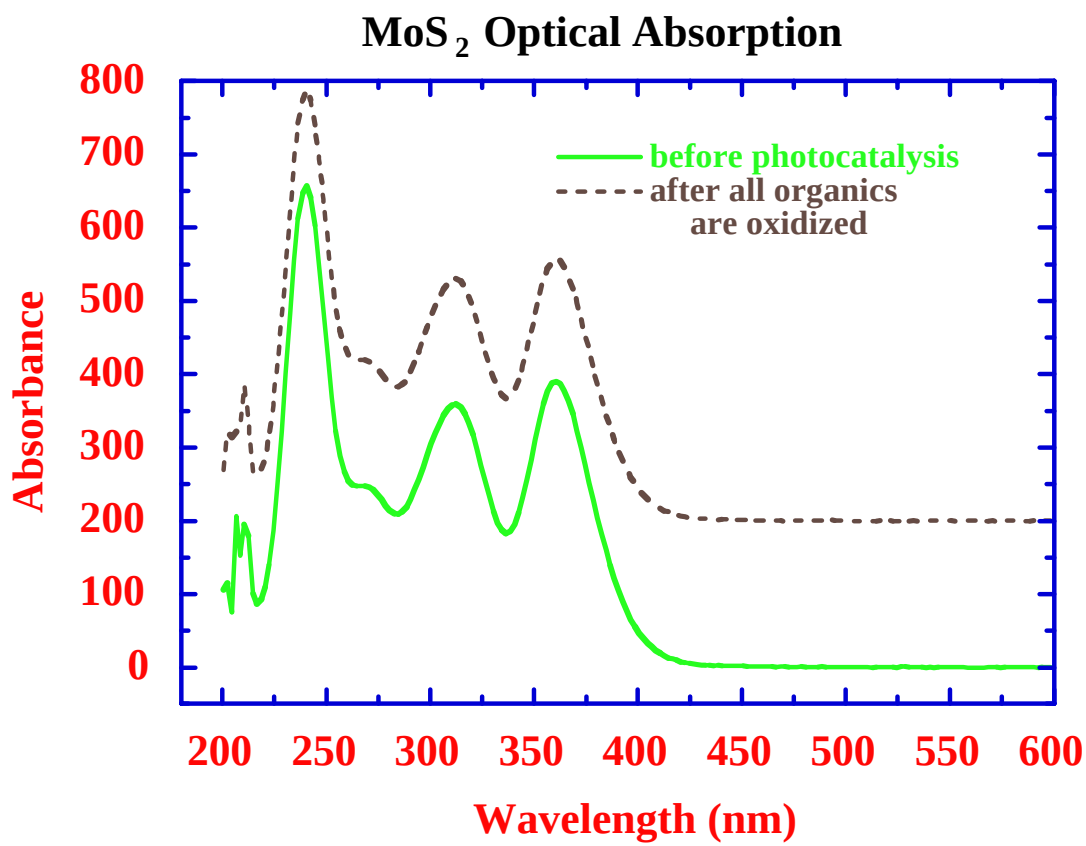
Basic Concept -

- 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 amounts 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.



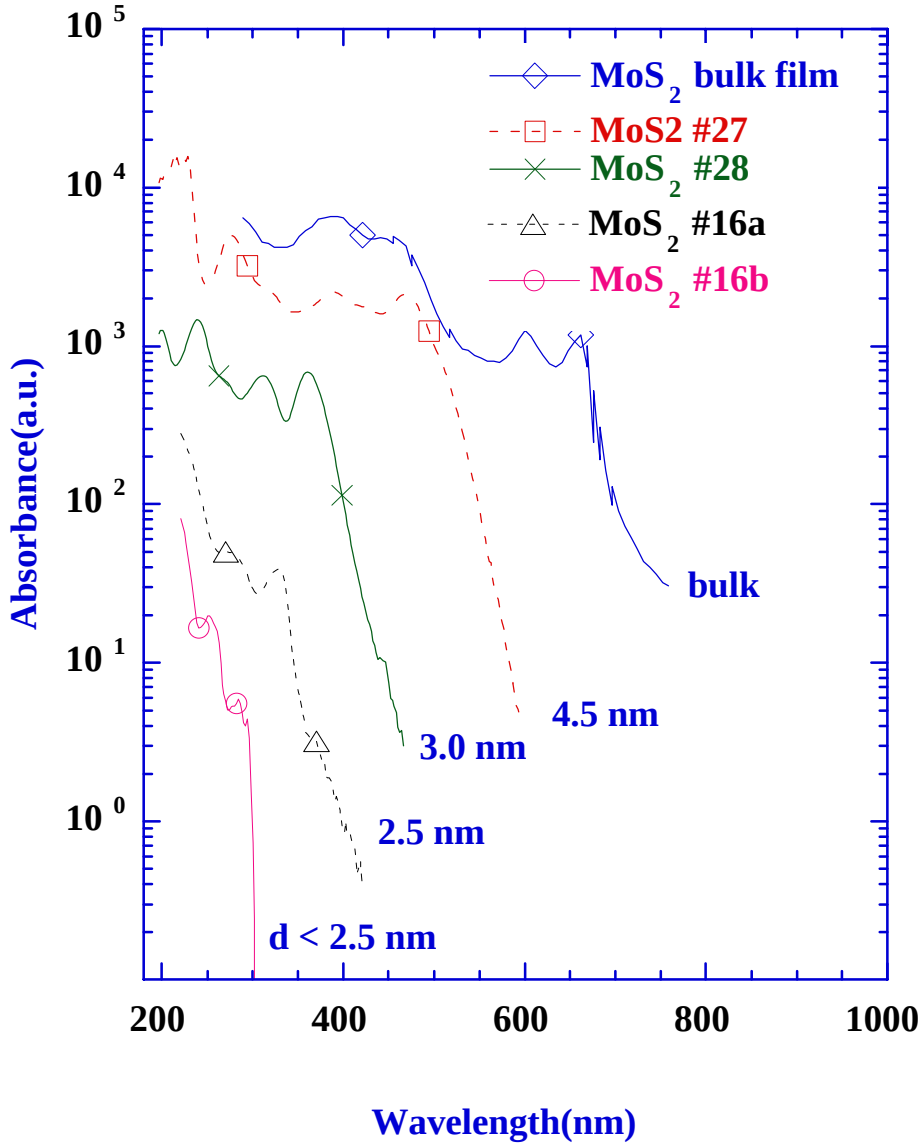
t = 4.15 min, MoS_2 nanocluster elution peak absorbance spectra -



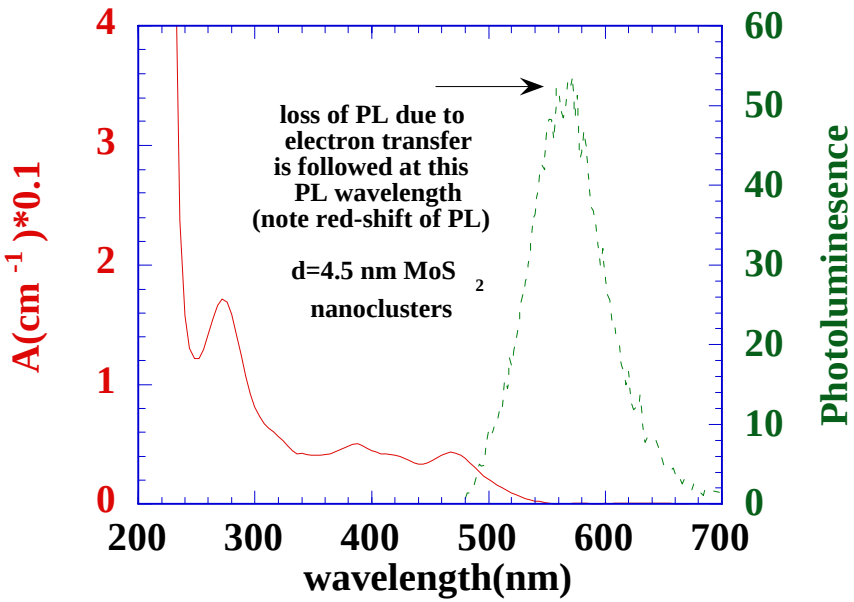
- No reduction in optical abosrbance, nanocluster concentration, or photocatalytic activity were observed.

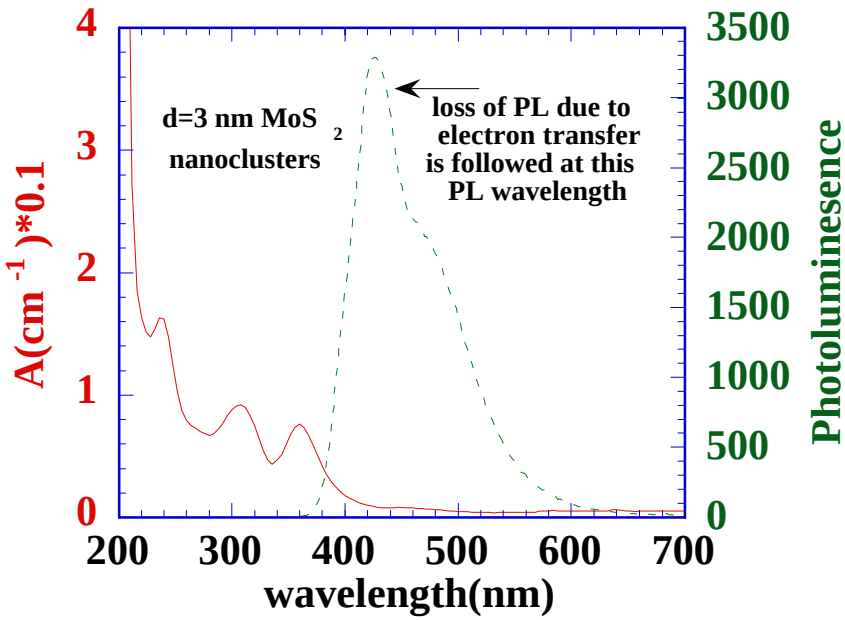
Tunable Bandgap Nanosize Semiconductors

- Due to quantum confinement of the carriers (electrons and holes) the bandgap of sufficiently small semiconductors depends on the size, as does the potential energy of the valence and conduction bands.
- The optical absorbance of nanosize MoS_2 is blue-shifted relative to the bulk.
- Can adjust light absorption properties by changing the size!



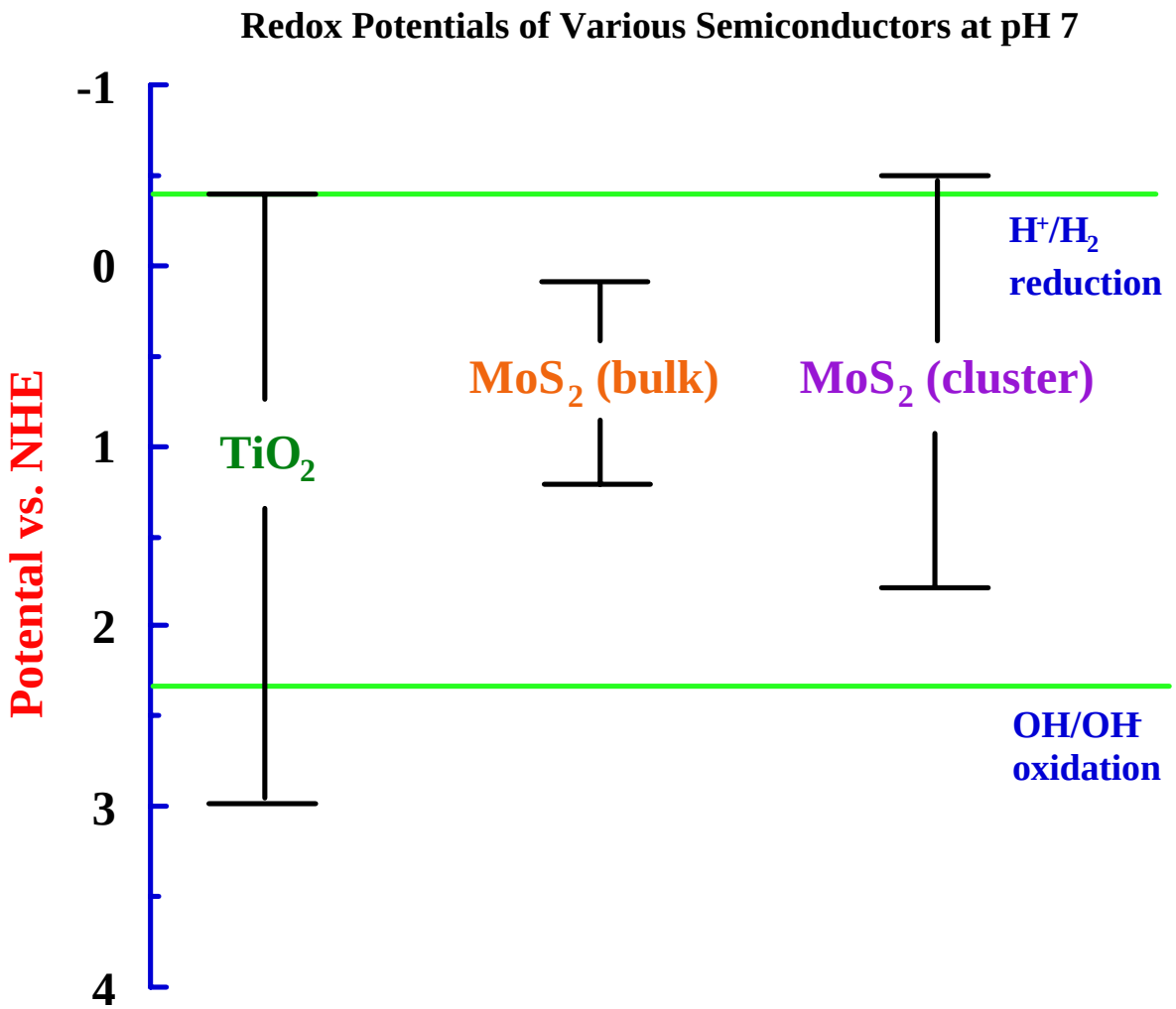
The Photoluminescence (PL) of nanosize MoS_2 also depends on size



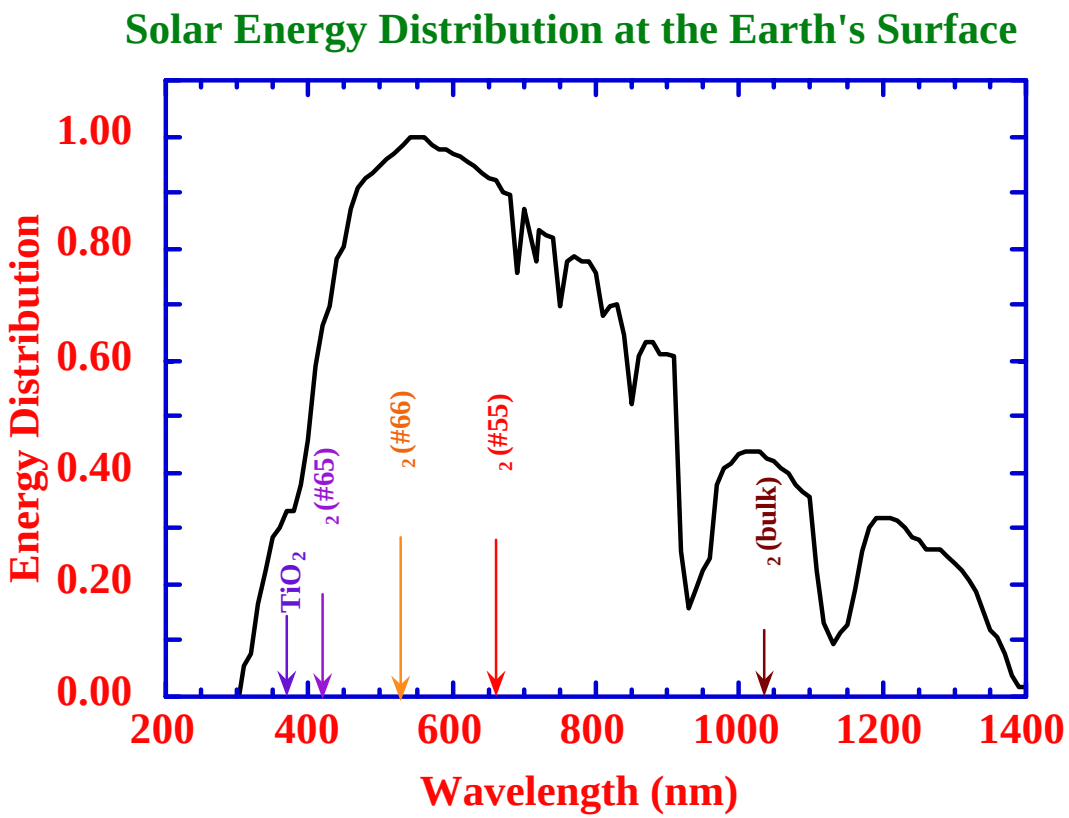


- Can use PL to monitor e-h transfer rates to organic molecules

The Oxidation and Reduction Potentials Shift with Decreasing Cluster Size

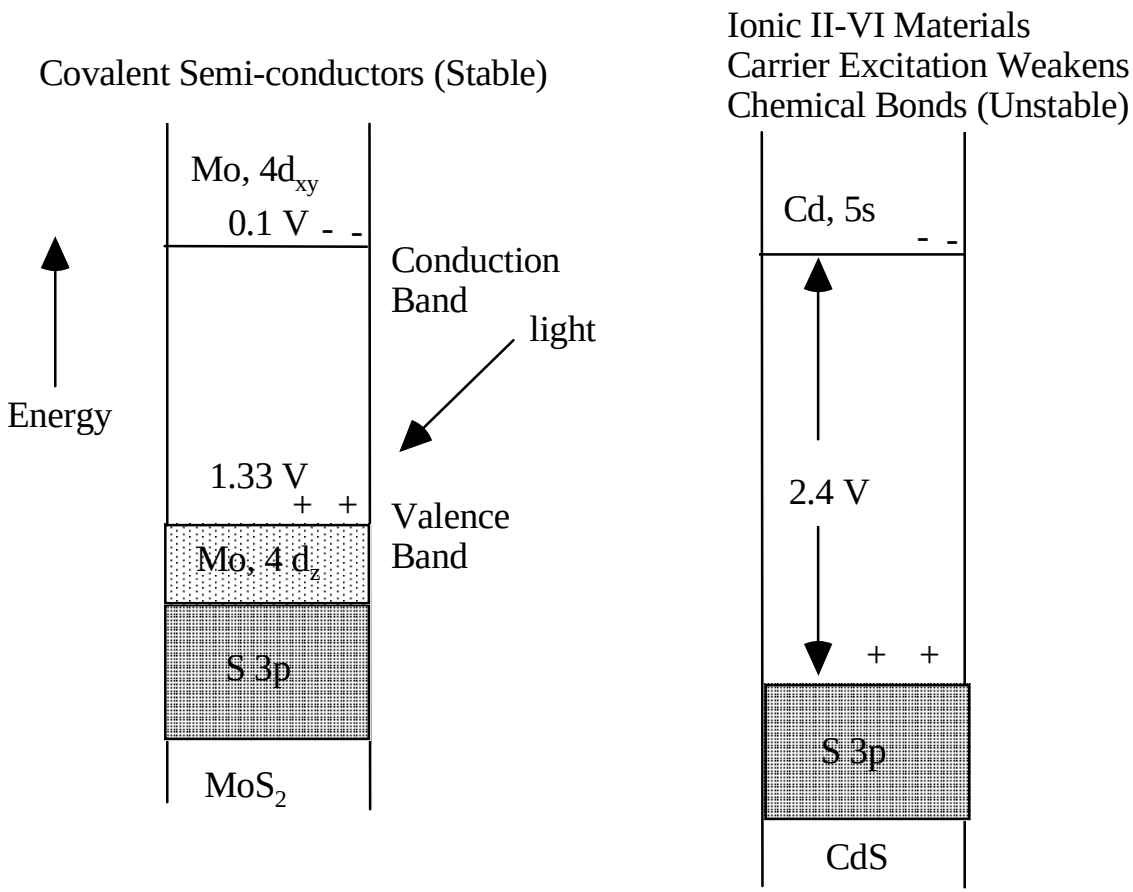


MoS_2 Cluster Size Determines Amount of Sunlight Absorbed



- Both light absorbance and redox potentials are chosen to optimize photooxidation rate.
- Mixtures of nanoclusters can be selected to span a range of absorbance and photooxidation potentials for a variety of chemicals.

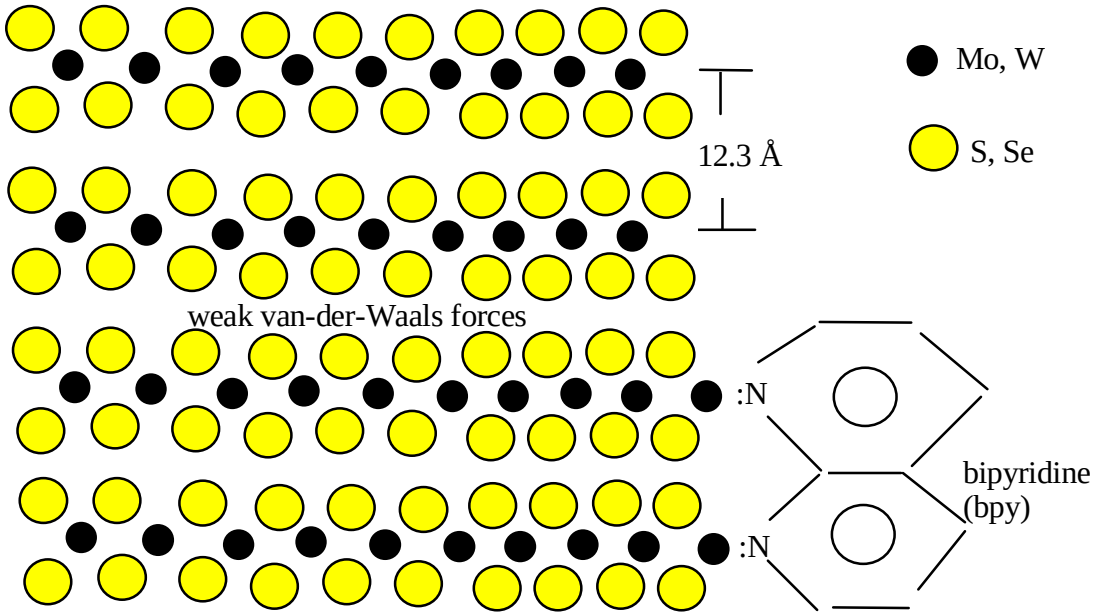
MoS_2, Like TiO_2 Has Exceptional Photostability



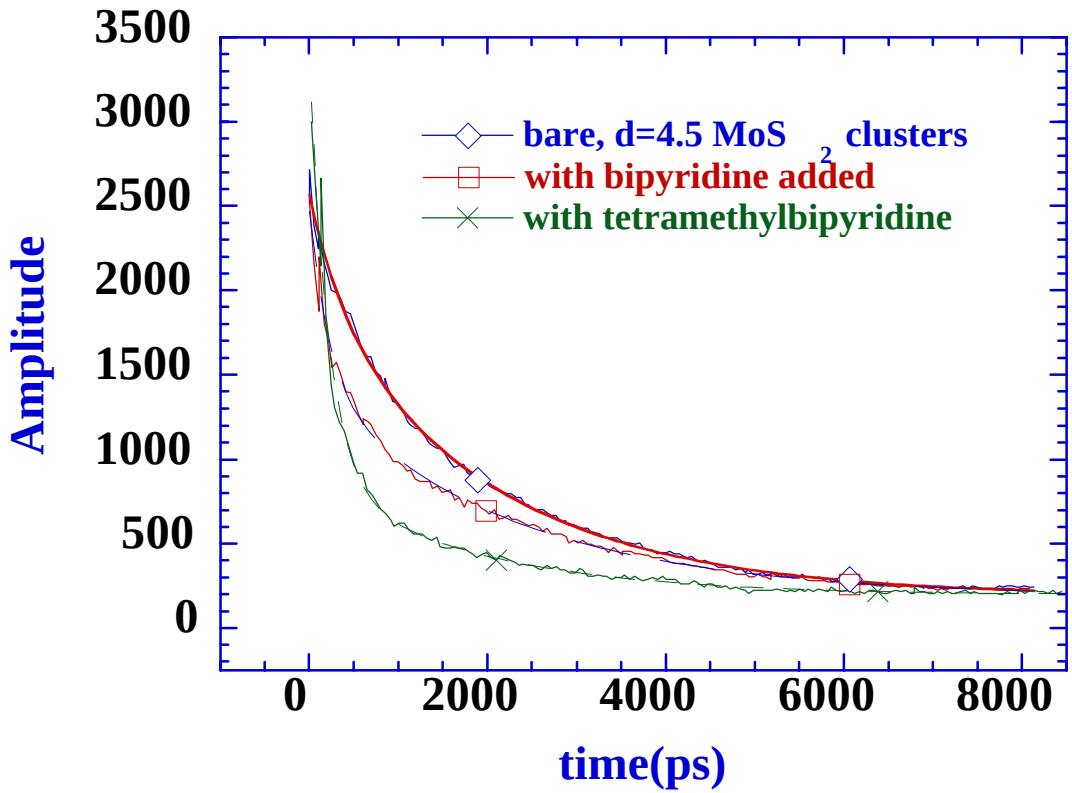
- Kinetic stability occurs because both valence and conduction bands are localized on the metal, so carrier excitation doesn't weaken any chemical bonds.

MoS_2 Layered Structure Allows Strong Binding of Organic Chemicals to Mo Edge Sites

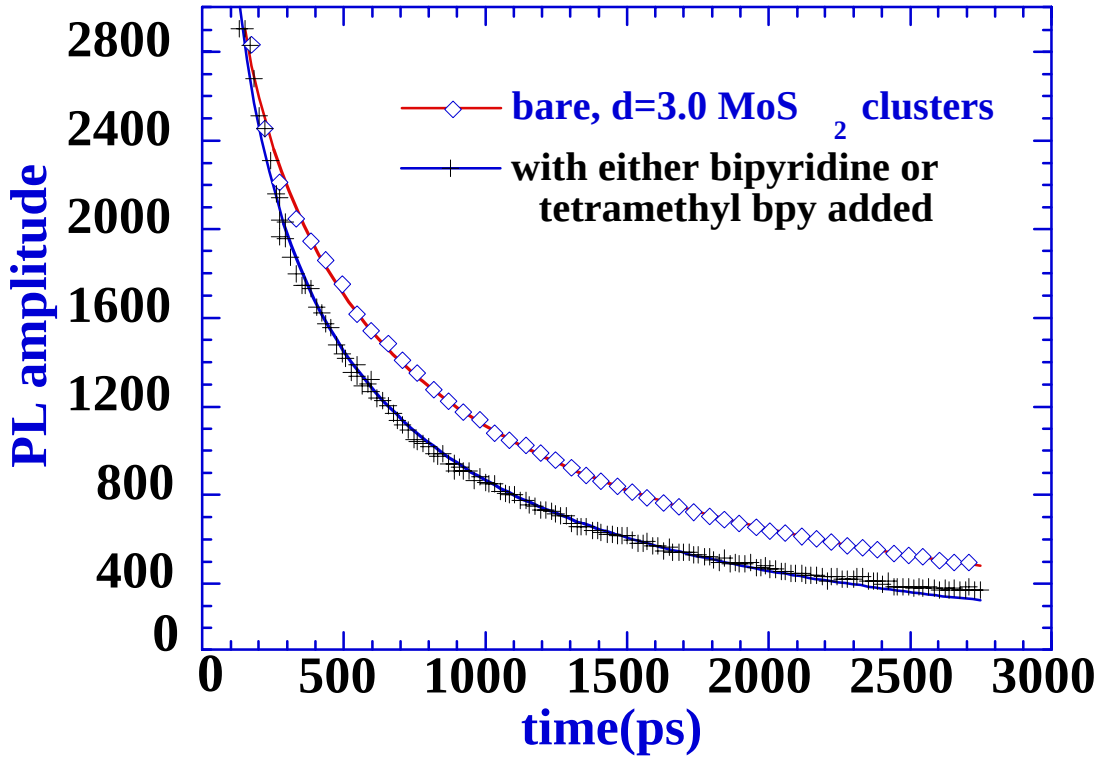
- If electron transfer (E.T.) to bpy occurs, the rate of carrier recombination on the MoS_2 nanocluster which produces visible PL is reduced.
- The more difficult a material is to reduce, the slower the E.T. rate (e.g. tetramethymethyl bpy vs. bpy)
- By following the kinetics of decay of the MoS_2 PL peak we can obtain these E.T. rates and also estimate the conduction band potential.
- Quantum confinement shifts the conduction band potential to more negative values and the valence band potential to more positive values as the bandgap opens up with decreasing size.
- This increasing bandgap provides the driving force for the photoredox reaction and increases destruction of the organic.
- A dramatic increase in the PL decay rate means a lot of E.T. is occurring!
- Similar considerations apply to hole transfer (oxidation) to an organic.



Effect of Size and Substrate Redox Potential on Electron Transfer (E.T.)



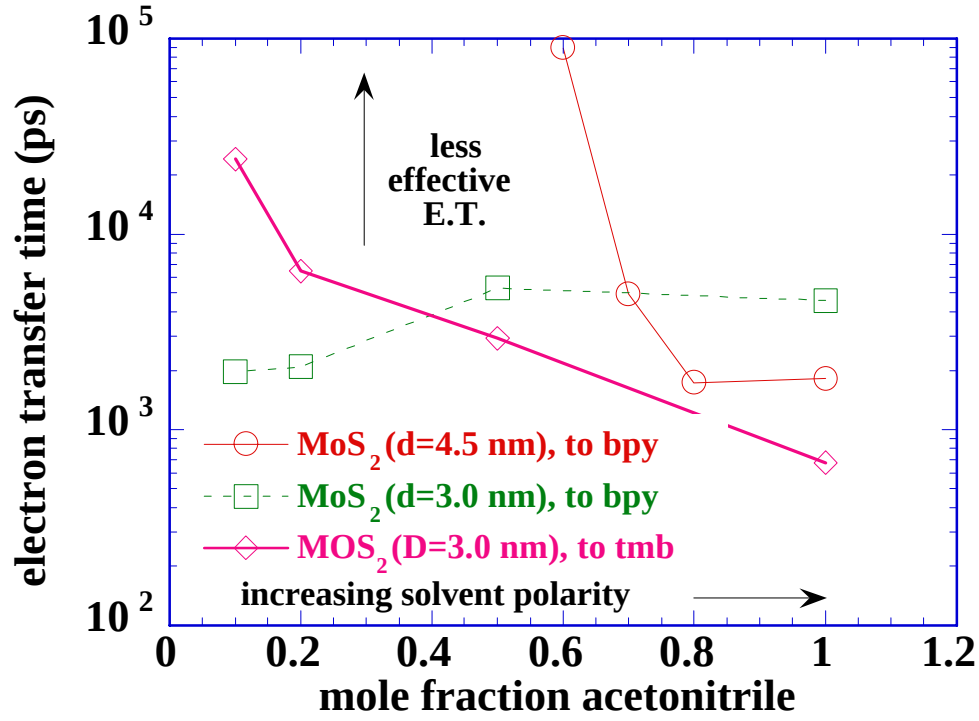
- The decay of the PL can be roughly described by, $I_{PL}(t) = e^{-(\Gamma_{PL}+\Gamma_{ET})t}$
- Larger nanoclusters absorb more visible light but have less driving force (free energy) for E. T.
- More difficult-to-reduce substrates (e.g. TMB vs. BPY), have slower kinetics.



- Smaller clusters (wider bandgap) absorb less light but can reduce a wider variety of organics at comparable reaction rates.

Effect of Solvent Polarity and Cluster Size on Electron Transfer (E.T.)

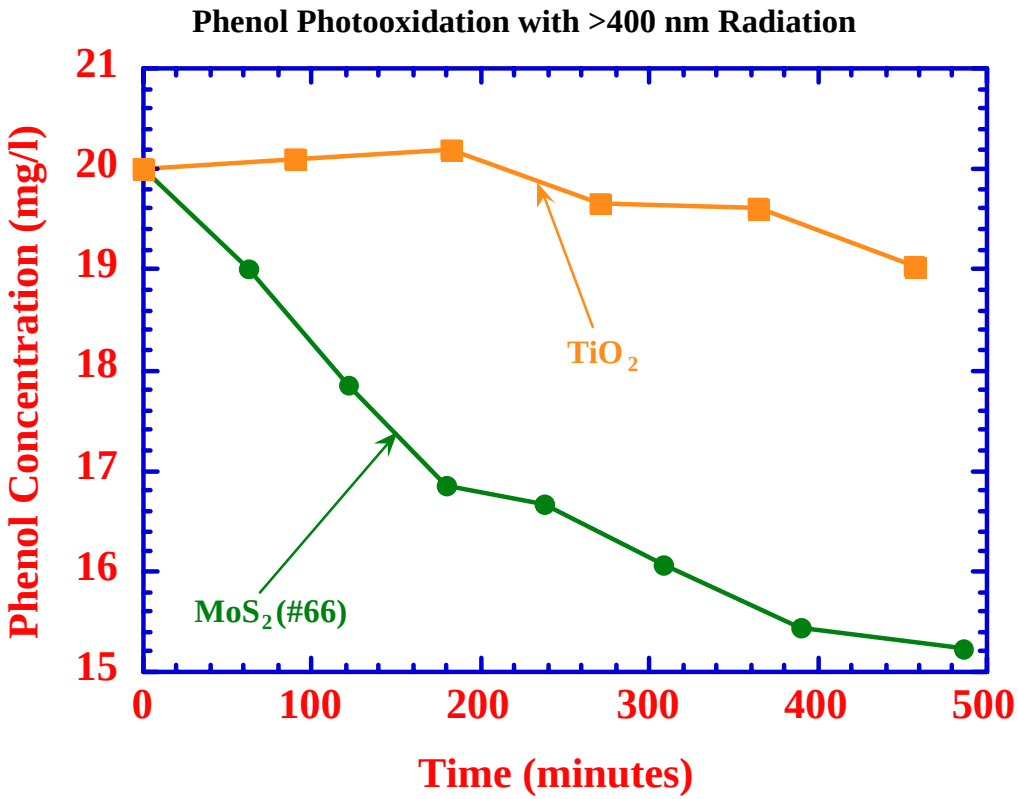
1) Use Benzene (non-polar)/Acetonitrile (polar) mixture.
2) Study two sizes of MoS_2 (with increasingly negative reduction potentials).
3) Study two organics (with increasingly negative redox potentials).



- Wide bandgap (bandege ~450 nm), d = 3.0 nm MoS_2 has sufficient overpotential to reduce bpy at a rate independent of solvent polarity. However, this rate slows down considerably with decreasing solvent polarity when the substrate (tmb) is more difficult-to-reduce.
- Larger, d = 4.5 nm MoS_2 (bandedge ~ 550 nm) only has enough overpotential to photoreduce bpy rapidly at high solvent polarities.

Our Photocatalytic Reactor

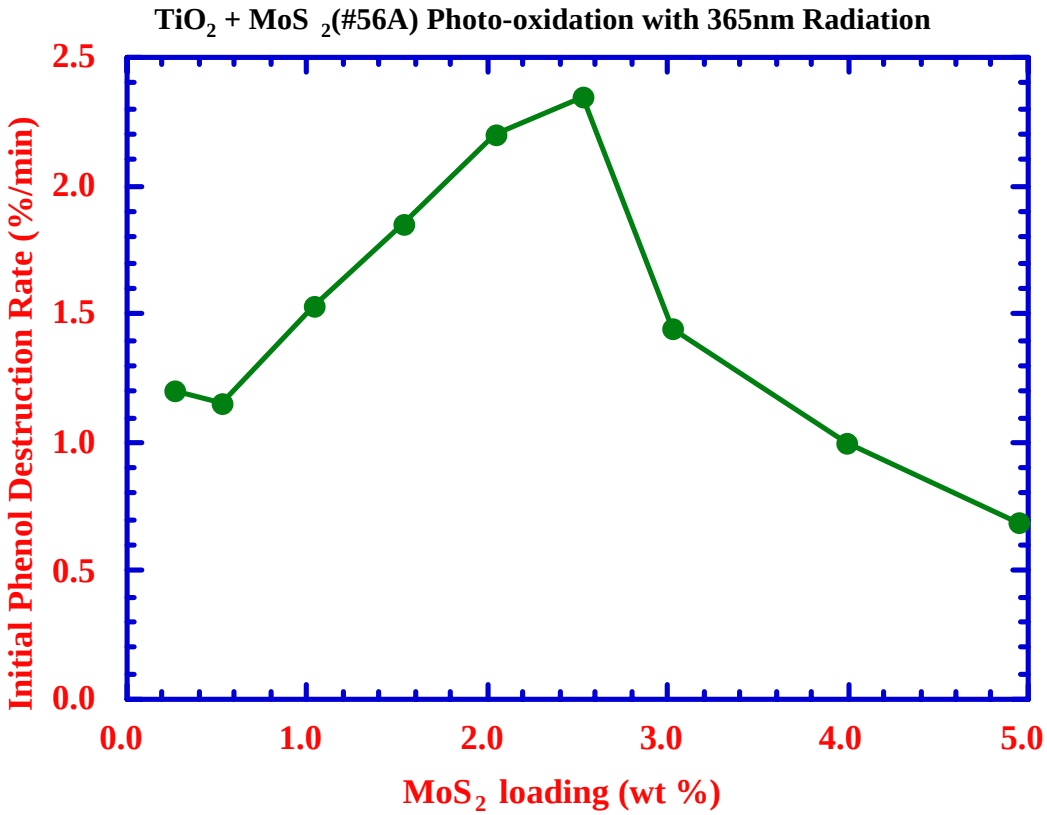
Photocatalysis of Phenol Using Dispersed Nanosize MoS_2



Significance -

- First photooxidation of phenol using <u>only</u> visible light and an entirely inorganic, photostable catalyst.

Photocatalysis of Phenol Using Nanosize MoS_2 Supported on TiO_2 Powder



- Light Absorbance by MoS_2.
- Carrier transfer between MoS_2 and TiO_2 support decreases recombination rate and increases photooxidation rate of organic.

Future Research Directions

- Improve nanocluster/support interactions by heat treatments after deposition of nanoclusters to further improve e-h transfer rates.

- 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.

- Develop better understanding of the factors that influence electron-hole transfer kinetics.

Conclusions

- Adjustment of the bandgap of nanosize MoS_2 can be used to tune the valence and conduction band potentials to optimize the destruction of an organic.

- Polar solvents like water or acetonitrile provide the most favorable electron transfer rates.

- Fully dispersed nanosize MoS_2 was shown to catalyze the destruction of an alkyl chloride using only visible light while maintaining its structure, catalytic activity, and optical absorbance properties.

- Both dispersed and supported nanoclusters of MoS_2 were shown to destroy a common organic pollutant, phenol, using only visible light.

Relevant Publications -

J. P. Wilcoxon, T. R. Thurston, and J. E. Martin, “Applications of Metal and Semiconductor Nanoclusters at Thermal and Photo-Catalysts,” to appear in Nanostructured Materials, 1998.

F. Parsapour, D. F. Kelley, and J. P. Wilcoxon, “Interfacial Electron Transfer in MoS_2 Nanoclusters,” J. Chem. Phys., submitted 1998.

T. R. Thurston and J. P. Wilcoxon, “Photo-oxidation of Organic Chemicals Catalyzed by Nanoscale MoS_2,” submitted to J. Phys. Chem, 1998.

J. P. Wilcoxon and S. A. Craft, “Liquid Chromatographic Analysis and Characterization of Inorganic Nanoclusters,” in NanoStructured Materials, Vol 9, pp. 85-88, 1997, Elesvier Science Ltd.

J. P. Wilcoxon, R. Parsapour, and D. F. Kelley, “Studies of Photoredox Reactions on Nanosize Semiconductors,” proceedings of the fourth international conference on Quantum Confinement: Nanoscale Materials, Devices and Systems, 119th meeting of the Electrochemical Society, Montreal, Quebec, Canada, May 4-9, 1997.

J. P. Wilcoxon, P. Newcomer, F. Parsapour, D. R. Kelley, “Studies of Photoredox Reactions in Nanosize Semiconductors,” proceedings of symposium Q, Fall MRS Society, Boston, MA, Dec 1-5, 1996.

J. P. Wilcoxon, P.P. Newcomer and G. A. Samara, “Synthesis and Optical Properties of MoS_2 Nanoclusters,” proceeding of Symposium Q, Fall MRS Society, Boston, MA, Dec 1-5, 1996.

J. P. Wilcoxon, P. Newcomer, G. A. Samara, “Synthesis and Optical Properties of MoS_2 and Isomorphous Nanoclusters in the Quantum Confinement Regime,” J. Appl. Phys., 81, 7937, (1997).

F. Parsapour, D. F. Kelley, S. Craft, and J. P. Wilcoxon, “Electron Transfer Dynamics in MoS_2 Nanoclusters: Normal and Inverted Behavior,” J. Chem. Phys., 104, 1, (1996).

J. P. Wilcoxon, G. A. Samara, and P. Newcomer, “Strong Quantum Confinement effects in Semiconductors: FeS_2 Nanoclusters,” Solid State Communications, 98, 581, (1996).

J. P. Wilcoxon and G. A. Samara, “Strong Quantum-Size Effects in a Layered Semiconductor: MoS_2 Nanoclusters,” 51, 7299, Physical Rev B, Rapid Comm. (1995).