

# Photooxidation of Organic Wastes using Semiconductor Nanoclusters

## First Year Research Highlights

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### Goal

The photooxidation of toxic organic chemicals to carbon dioxide and dilute mineral acids using sunlight as an energy source and nanosize semiconductors to catalyze the process.

### Introduction

Our efforts in the first year of this program focused on demonstration of three important attributes of nanosize  $\text{MoS}_2$  as used to photocatalyze the oxidation of organics in solution: (1) Ability to utilize visible light to initiate photo-redox reactions in solution. (2) Successful oxidative destruction of organic pollutants. (3) Structural and chemical integrity during and after the removal of organic pollutants (i.e. no photochemical degradation of the catalyst).

To these ends we have used nanosize  $\text{MoS}_2$  of three different sizes and associated band gaps, and studied photoredox reactions catalyzed with nanosize  $\text{MoS}_2$  that had been both dispersed in solution and supported on a macroscopic powder. The latter would be the method of choice for use in practical photocatalytic applications.

As we emphasized in our original proposal,  $\text{MoS}_2$  in nanosize form can be tuned to absorb various amounts of the solar spectrum. In figure 1 we show the relationship of the absorption edge of the various materials studied as photocatalysts relative to the natural solar spectrum.

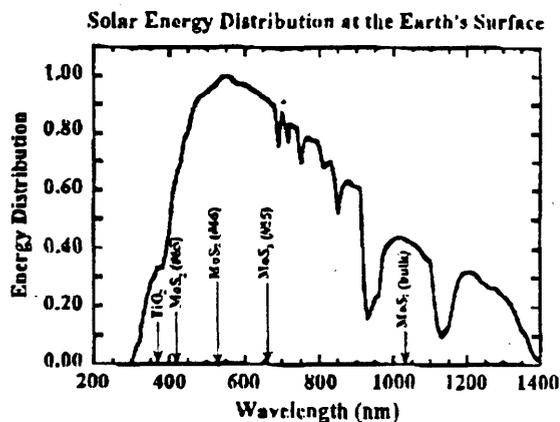


FIG. 1. Energy distribution of the solar radiation that reaches the earth's surface as a function of photon wavelength (AM1.5). The band gap wavelengths of various semiconductor compounds are also shown.

### Room Temperature Photo-redox Reactions

We have demonstrated electron and hole transfer from nanosize  $\text{MoS}_2$  using visible light. In order to oxidize organic impurities using this part of the spectrum we needed to add an agent, bypyridine (bpy), which could accept an elec-

tron and be reduced. In actual applications we anticipate the use of a sacrificial electron acceptor played by the bpy could be replaced by soluble heavy metal ion pollutants, (e.g. Pb, Cd, **Fig**) which, when reduced, would precipitate out of solution, thus purifying the water and driving the reaction. Using liquid chromatography analysis we have demonstrated that bypyridine binds strongly to nanosize  $\text{MoS}_2$  and acts like an electron transfer relay to effect charge separation. The hole left behind on  $\text{MoS}_2$  is then used to oxidize the organic impurities. In its reduced form bypyridine complexes to the oxidized organic impurity and precipitates out of solution. We studied the chemistry of this process by high pressure liquid chromatography which separates each of the chemicals in the solution from the  $\text{MoS}_2$  photocatalyst. The results of this experiment are shown in figure 2. The initially present organic impurity peak at  $t=5.2$  minutes (an organic chloride) is destroyed as more bypyridine is added until it cannot be detected. However, the amount of nanosize  $\text{MoS}_2$  remains unchanged, as measured by the area under the  $\text{MoS}_2$  elution peak. Another, broader, organic peak observed in this figure at  $t=4.7$  minutes also is destroyed by the  $\text{MoS}_2$  as additional bpy is added, and, at higher levels of bpy (not shown) this chemical is completely oxidized and precipitated out of solution as well. The white precipitate which forms can be removed from the solvent.

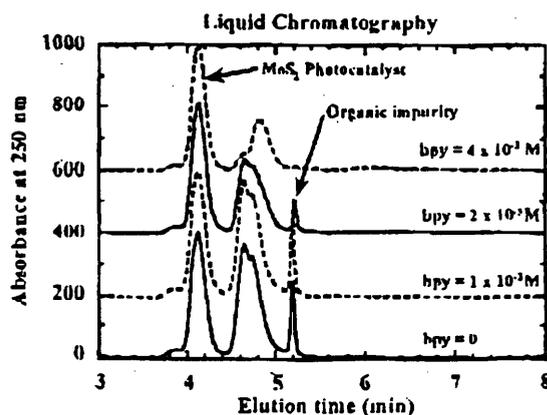


FIG. 2. Plot of optical absorption at 250 nm (a measure of the organic concentration) vs. elution time for impurity chemicals and  $\text{MoS}_2$  nanoclusters. The organic impurities shown were photooxidized by the  $\text{MoS}_2$  nanoclusters which have bypyridine (bpy) added to them. A new complex of the reduced bypyridine and oxidized organics is formed (see new elution peak at the upper trace) and due to its limited solubility it precipitates and is removed from the solution.

Studying the spectral properties of  $\text{MoS}_2$  before and after the reaction shows that it has not changed in size, concentration, or photoproperties. The absorption spectrum of the  $\text{MoS}_2$  photocatalyst is shown in figure 3. Remarkably, the above photoredox reaction occurs rapidly (e.g. <1 minute) under ordinary room light (laboratory illumination) using these 3 nm nanoclusters which begin absorbing light at 450 nm. For larger 4.5 nm  $\text{MoS}_2$  which begin absorbing light near 550 nm, the reaction is significantly slower and less complete under room illumination. We attribute this to the narrower band gap and correspondingly lower reduction potential of these larger nanoclusters, which provides less of a driving force for electron transfer to bpy. For these larger clusters, a stronger radiation source may be required to achieve complete photooxidation.

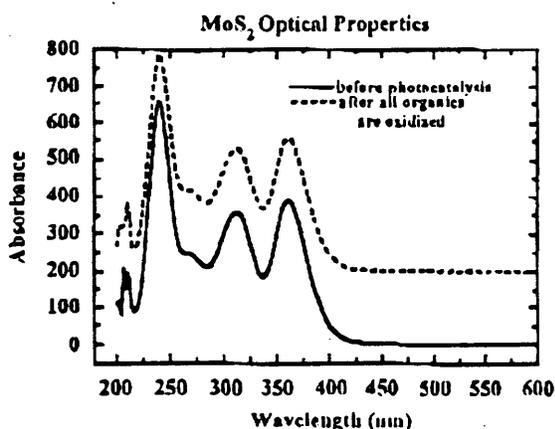


FIG. 3. Plot of optical absorption vs. wavelength for nanosize  $\text{MoS}_2$  before and after photo-oxidation and precipitation of organic contaminants. No changes in either size or structure of the  $\text{MoS}_2$  was observed. (The dashed curve has been shifted vertically for clarity).

**Significance:** This is the first demonstration of photoredox reactions to completely oxidize and precipitate organics from solution using nanosize semiconductors and weak visible light as the initiator. Furthermore, using chromatography we have been able to follow the course of the photochemistry and demonstrate that the nanosize  $\text{MoS}_2$  used is unaltered by the reaction - it functions as a true photocatalyst.

### Time-Resolved Electron and Hole Transfer Studies (D.F. Kelley, Colorado State)

During our first year, progress has been made in understanding the interfacial charge transfer dynamics in  $\text{MoS}_2$  nanoclusters. These nanoclusters are synthesized using the methods developed at SNL, and are subsequently placed in other solvent environments. The dynamics are then studied using time-resolved laser spectroscopy. These studies may be divided into two categories: first, studies of hole transfer to iodide and triiodide ions; and second, studies of electron transfer in  $\text{MoS}_2/\text{TiO}_2$  nanoclusters. The results obtained in both categories are still preliminary; further studies of this type constitute a major portion of the work planned for the second year of the program.

We have found that emission from electron/hole trap states is significantly quenched by the presence of  $\text{I}^-$  or  $\text{I}_3^-$

ions. Time-resolved studies show that this quenching results from a reduction of the excited state lifetime. The extent of lifetime reduction was found to increase with  $\text{I}^-$  concentration, and is assigned to interfacial hole transfer. Present studies are aimed at determining the bimolecular rate constants for this process and their energy dependence. These hole scavengers ( $\text{I}^-$  and  $\text{I}_3^-$ ) were chosen because of their electrochemical oxidation potentials, and the resulting exothermicity of the reaction. The following considerations are relevant. The redox potential for the process  $\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$  is 0.534 V vs. NHE. However, oxidation of  $\text{I}^-$  by the nanocluster hole will initially produce an iodine atom, and the  $\text{I}_2$  bond dissociation energy (1.494 eV) must be taken into account. Thus, the oxidation potential for the process  $\text{I}^- + h\nu \rightarrow \text{I}$  is estimated to be about +1.28V. This must be compared to the redox potential of the top of the  $\text{MoS}_2$  valence band. This potential is about +1.22V for bulk material, and on the basis of an effective mass model, is estimated to be about +1.42V in these quantum-confined nanoclusters. Thus, the charge transfer driving force is about 0.14 eV from the valence band and correspondingly less from hole trap states. Only slightly more favorable energetics are calculated for the triiodide ion. The conclusion which results from these measurements and calculations is an important one: hole transfer occurs fairly rapidly and competes with electron/hole recombination, even though the driving force is rather small.

We have also obtained preliminary results on  $\text{MoS}_2$  nanocluster to  $\text{TiO}_2$  particle electron transfer. In these studies, samples of  $\text{MoS}_2$  nanocluster are simply mixed with the  $\text{TiO}_2$  particles, and some adhesion between the different types of particles occurs. The nature of these hybrid particles has not yet been characterized. However, we find that following photoexcitation of the  $\text{MoS}_2$ , the presence of the  $\text{TiO}_2$  quenches the emission, while the emission decay kinetics remain unaffected. The most plausible interpretation of this result is that electrons in the  $\text{MoS}_2$  conduction band may either transfer to the  $\text{TiO}_2$  particle or become trapped, and that the trapped electrons undergo little or no electron transfer. Since this partitioning occurs very rapidly and only trap state emission is observed, there is no effect on the observed kinetics. This result suggests that passivation of the  $\text{MoS}_2$  electron traps may dramatically improve the efficiency of  $\text{TiO}_2$  sensitization. Electron transfer quantum yield measurements, and efforts to passivate the electron traps are currently in progress.

### Photocatalytic destruction of Phenol Using nanosize $\text{MoS}_2$ on $\text{TiO}_2$ powder.

In these studies our desire was to demonstrate improved destruction of a difficult-to-oxidize material, phenol, using nanosize  $\text{MoS}_2$ , both alone and supported on the best available  $\text{TiO}_2$  powder catalyst, Degussa P-25.

Figure 4 compares the photocatalytic activity for phenol destruction of  $\text{MoS}_2$  nanoclusters and Degussa P25  $\text{TiO}_2$  (this commercially available  $\text{TiO}_2$  is generally regarded as the standard for comparing the photocatalytic activity among different materials, since absolute quantum efficiencies are extremely difficult if not impossible to measure because of scattering effects). The plot shows phenol concentration as a function of time when the sample is irradiated by a 450 watt arc lamp combined with a 455 nm high pass filter. This filter transmits less than 0.1% of the incident light at 400

nm, 50% at 455 nm, and 97% at 500 nm. Comparison to the solar spectrum in figure 1 shows that this filter roughly approximates the solar spectrum in the crucial 400 to 500 nm region. The phenol concentration was determined from high pressure liquid chromatography (HPLC) measurement. on -1 ml samples removed from the irradiated solution at various times. The central feature of figure 4 is that the  $\text{MoS}_2$  nanoclusters readily destroy phenol with  $>400$  nm photons. while  $\text{TiO}_2$  does not.  $\text{MoS}_2$  nanocluster will therefore be more active than  $\text{TiO}_2$  when irradiated by the sun.

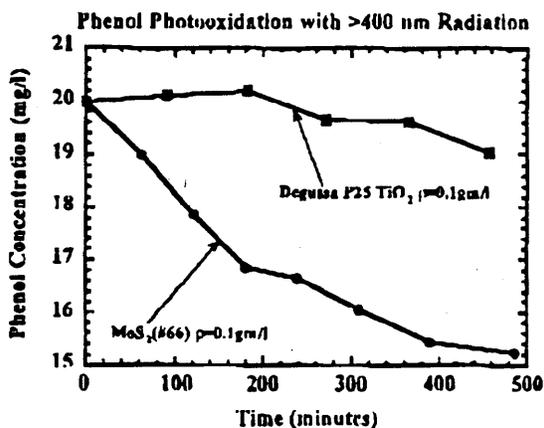


FIG. 4. Phenol destruction with  $>400$  nm radiation and two different catalysts. Under these conditions, the phenol is readily destroyed with the nanoscale  $\text{MoS}_2$  catalyst, but not with the  $\text{TiO}_2$ .

Practical nanoscale catalysts must be deposited onto a support material, so data such as that presented in figure 4 is only of academic interest. Preliminary experiments have been performed where nanoclusters are deposited on a number of support materials. The most promising results so far have been studies of nanoscale  $\text{MoS}_2$  deposited on Degussa P25  $\text{TiO}_2$ . In this case electron transfer may occur between the  $\text{MoS}_2$  and  $\text{TiO}_2$  semiconductors, which would greatly decrease electron-hole recombination rates, and thereby increase catalytic activity. Figure 5 shows the rate of phenol destruction for equal masses of P25  $\text{TiO}_2$  alone and P25  $\text{TiO}_2$  loaded with less than 0.9 weight percent of  $\text{MoS}_2$  (#55) nanoclusters (the actual loading is probably about 0.2 wt. %, though it has not been measured yet). Under these conditions Degussa  $\text{TiO}_2$  is an effective photocatalyst as shown. More impressively, deposition of a scant 0.9 wt% of 8-10 nm  $\text{MoS}_2$  enhances the catalytic; destruction of phenol significantly. Since typical catalyst loadings are  $\sim 5\%$ , this enhancement of activity is very encouraging. Experiments where  $\text{MoS}_2$  nanoclusters are deposited under varying conditions onto many other kinds of substrates are in progress.

## Future Directions

We have developed new synthetic strategies for photocatalysts including formation of nanosize  $\text{MoS}_2$  directly on support materials such as  $\text{TiO}_2$  and chemical modification of  $\text{MoS}_2$  using metals such as Pt and  $\text{RuO}_2$  to improve its activity. We will pursue these approaches as well as continue our well-developed testing procedures to evaluate the best photocatalysts for destruction of a wide range of organic pol-

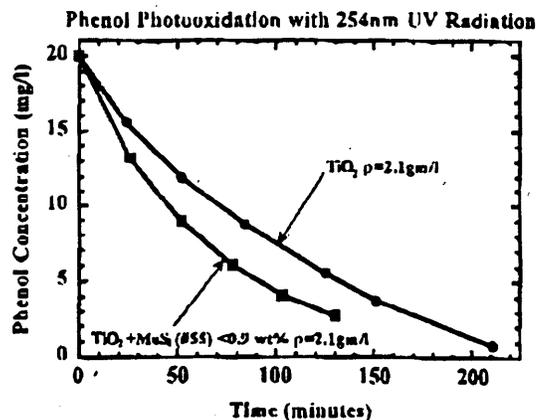


FIG. 5. Phenol destruction with 250 nm radiation and two different catalysts. The  $\text{TiO}_2$  alone effectively catalyzes the reaction at this wavelength, however, the addition of less than 0.9 weight percent  $\text{MoS}_2$  nanoclusters increases the reaction rate considerably.

lutants in water. We will extend our studies to include nanosize  $\text{WS}_2$  and combinations of  $\text{MoS}_2$  with  $\text{WS}_2$ . D.P Kelley will be continuing his studies of electron and hole transfer using time-resolved PL and absorption to better understand the chemical and structural features which influence high photocatalytic activity in nanosize  $\text{MoS}_2$  and  $\text{WS}_2$ .

## Interactions

The results and experience of our BES program to investigate thermal catalysis and photosynthetic uses of nanosize  $\text{MoS}_2$  and  $\text{WS}_2$  aid us in designing better photoredox catalysts. We also have internally funded efforts to study films of  $\text{MoS}_2$  nanoclusters as micromachine lubricants, and as sprayable coatings.

## Publications

J.P. Wilcoxon, P.P. Newcomer, and G.A. Samura, "Synthesis and Optical Properties of  $\text{MoS}_2$  and Isomorphous Nanoclusters in the Quantum Confinement Regime, *J. Appl. Phys.*, 81, 7934, (1997).

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

J.P. Wilcoxon, K. 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-F. 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<sub>2</sub>** Nanoclusters", proceeding of Symposium Q, Fall MRS Society, Boston, MA, Dec. 1-5, 1996.

## **Presentations**

J.P. Wilcoxon, Chromatographic Characterization of Metal and Semiconductor Nanoclusters, MRS Meeting, Boston, MA, Dec. 1997.

J. P. Wilcoxon, B. Hance, D. Strall, and W. Chambers, "Direct Elemental Analysis of Inorganic Nanoclusters in Organic Solvents Using Graphite Furnace AA, 39th Rocky Mountain Conference on Analytical Chemistry, Aug. 3-7 1997, Denver, Co.

J.P. Wilcoxon, R. Parsapour, and D.F. Kelley, "Studies of Photoredox Reactions on Nanosize Semiconductors", 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, G. A. Samara, and P. Newcomer, "Synthesis and Optical Properties of **MoS<sub>2</sub>** Nanoclusters in the Strong Quantum Confinement Regime", Symposium Q, 1996 meeting of the MRS Society, Boston, MA.

J-P. Wilcoxon, F. Parsapour, and D.F. Kelley, "Studies of Photoredox Reactions on Nanosize Semiconductors", Symposium Q, 1996 meeting of the MRS Society, Boston, MA.