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Photooxidation of Organic Wastes Using Semiconductor Nanoclusters

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Research Objective

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

Research Progress and Implications

This report summarizes work after 1.5 years of a 3-year project. Our efforts have focussed on demonstration of photocatalysis of organic pollutants using nanosize MoS_2. We investigated the effects of :1)bandgap, valence and conduction band energies; 2)surface modification of MoS2 by deposition of metal and metal oxide islands to enhance electron transfer; and 3)use of semi-conductor semi-conductor composites to achieve improved charge separation and thus photooxidation of pollutants.

We synthesized and studied nanosize MoS_2 of three different sizes and associated bandgaps and studied photoredox reactions of nanosize MoS_2 dispersed in solution and supported on a macroscopic powder. The latter would be the method of choice for use as a practical photocatalyst for water purification.

As we emphasized in our original proposal, MoS_2 in nanosize form can be tuned to absorb various amounts of the solar spectrum. We discovered there is an optimal choice of absorbance characteristics and valence and conduction band levels which allow the rapid photo-oxidation of a chosen organic molecule. The advantages of having a photostable material with a tunable bandgap were demonstrated in an experiment where phenol destruction with visible (>450 nm) light occurred at a dramatically faster rate with nanoscale MoS_2 catalysts compared to the best available previous material TiO_2. This was the first demonstration of rapid photooxidation of an organic molecule using a completely photostable catalyst and only visible light.

The possibility of transferring electrons or holes between nanoscale MoS_2 and other semiconductor materials in order to increase electron/hole lifetimes were explored. It was shown that small amounts (<5 weight %) of nanoscale MoS_2 deposited on to TiO_2 can lead to significant (~2) enhancements of phenol destruction rates.

Room Temperature Photo-redox Reactions: A number of different chemicals were photocatalyzed sucessfully to CO_2, but most of our work centered on the destruction of phenol. This particular organic was chosen for its ease of detection and relative resistance to oxidation, and because its photo-oxidation has been studied extensively by many previous researchers. No attempts were made to find the absolute quantum yield of the photo-oxidation process. Rather, following the approach of Serpone and coworkers we compared the relative activity of nanoscale MoS_2 to a well studied photocatalyst, Degussa P25 TiO_2.

Chemical analysis was done with high pressure liquid chromatography (HPLC) using a reverse phase column, Hewlett-Packard 1050 diode array detector, and Hewlett-Packard 1046A fluorescence detector. The fluorescence detector allowed detection of phenol to ~10 ppb without preconcentration. We were typically able to destroy phenol and certain cholorinated hydrocarbons such as pentachlorophenol (a common wood preservative) to undetectable levels in less than 2-3 hours of treatment.

A. Phenol Destruction With Visible Light

One of our primary reasons for examining MoS_2 nanoclusters was to try and find a nanoscale photocatalyst that is active when illuminated by visible radiation. We were quite successful in this

regard. MoS_2 nanoclusters could photocatalyze the destruction of a difficult-to-oxidize compound with visible light. The fact that both the 8-10 nm MoS_2 with a 700 nm bandgap and 4.5 nm MoS_2 with a 540 nm bandgap samples are catalytically active suggests that their valence bands are sufficiently low to produce hydroxyl radicals that then oxidize phenol. 3.0 nm MoS_2 with a bandgap of 420 nm was also effective but required light in the range 360-420 nm to work efficiently.

B. MoS_2 Supported Catalysts

Catalytic materials are often times deposited on to support materials. This is done not only to prevent the catalyst from agglomerating, but often times because reaction rates can be synergistically increased through interactions between the catalyst and support material. Semiconductor photocatalysts are no exception to this behavior, and for MoS_2 nanoclusters, deposition on a support material may prevent adverse chemical changes as well. Another twist in this vein for semiconductor photocatalysts is the possibility of electron or hole transfer between two semiconductor catalysts, which we have recently shown (see below) leads to enhanced electron-hole lifetimes, and faster reaction rates.

A series of experiments where 8 nm MoS_2 nanoclusters with a bandgap of ~700 nm were deposited on to powders TiO_2, SnO_2, WO_3, and ZnO were performed. The deposition method was remarkably simple. Powdered support material was mixed into a solution of MoS_2 nanoclusters and then centrifuged with a vacuum applied. The solution slowly evaporated leaving nanoclusters deposited on to the support material. No heating or other treatments were performed, so further enhancement of contact interactions between the nanoclusters and semiconductor support material is possible (see future directions). In all cases, between 0 and 6 weight percent MoS_2 nanoclusters were deposited on to the support. The reaction rate for destruction of 20 mg/l phenol was then measured with a total (MoS_2^+ support) catalyst density of 2 gm/l.

We found that MoS_2 nanoclusters had a significant enhancement of catalytic activity under the conditions described above, when deposited onto TiO_2. The other metal oxide powders were much less effective, and most showed some photodegration themselves-which may rule them out as practical support materials. . The destruction rate was enhanced up to a factor of ~2 when the loading was ~2.5 weight percent. When the 8 nm sized MoS_2 was not loaded on to TiO_2, however, the phenol destruction rate was much smaller than the enhancement achieved when it is loaded. These observations strongly suggest that electron or hole transfer is occurring between the TiO_2 and nanosize MoS_2. We hypothesized in our original proposal that we could take advantage of this synergism to enhance pollutant destruction rates significantly, and we have now established this fact.

The decrease in the reaction rate for loadings greater than 2.5 weight percent of nanosize MoS_2 is somewhat puzzling. There are apparently two competing processes occurring when 8 nm MoS_2 is loaded on to TiO_2, one which enhances phenol destruction and another which impedes it. A possible scenario which would explain this data is that a small amount of nanosize MoS_2 enhances phenol destruction through electron or hole transfer processes, but that excess amounts of MoS_2 impede phenol destruction by blocking important phenol binding sites on the TiO_2 surface. This has given us new ideas for support materials for nanosize MoS_2 (see future directions).

Time-Resolved Electron and Hole Transfer Studies

During this period we have focused on the study of interfacial electron transfer in hybrid semiconductor nanoclusters. Specifically, the MoS_2/TiO_2 and WS_2/TiO_2 hybrid nanoclusters have been synthesized and studied. The dynamics were studied using time-resolved laser spectroscopy.

The MoS_2/TiO_2 or WS_2/TiO_2 hybrid nanocluster emission kinetics were compared to those of the appropriate control, lacking TiO_2. In all cases, the kinetics consist of a very fast component and a slower, nonexponential component. The fast and slow components are assigned to electron/hole recombination from deep and shallow traps, respectively.

In the WS_2 case, the presence of the TiO_2 reduces the t=0 emission intensity, and results in a somewhat faster decay of the slow component. The decrease in the t=0 emission, along with a decrease in the total emission intensity, may be interpreted in terms of electron transfer from the WS_2 conduction band, prior to electron trapping. These processes are very fast. In other systems, trapping has been shown to occur on the sub-picosecond timescale. These results suggest that electron transfer from the conduction band occurs on a similar timescale. The increase in the decay rate of

the slow component may be interpreted in terms of electron transfer from the shallow traps. This electron transfer occurs on a much slower 10's of ps timescale, the same timescale as trapped electron/hole recombination. Little or no change is observed in the fast component, suggesting that electron transfer does not occur from the deep traps. These effects are fairly small, but quite reproducible, with the quantum yield for electron transfer being only about 20%. The implication is that we can dramatically improve electron transfer rates with these hybrid systems.

Planned Activities

The key to viable use of sunlight to destroy organic pollutants in water systems is significant and continuous improvements in our nanosize MoS_2 photocatalysts via pre-treatment and or chemical modification. We intend to study the effect of heating our MoS_2/ TiO_2 semiconductor hybrid nanoclusters to increase physical contact between the semiconductors and thus increase electron/ hole transfer rates. New chemical modifications to the surface of the nanosize MoS_2 will also be explored. By analogy with highly active MoS_2-Co/Ni hydrotreating catalysts, we intend to deposit islands of base metals such as Co, Ni and Fe on nanosize MoS_2 and investigate the photocatalytic behavior.

Another key idea we will explore is the use of nanosize MoS_2 supported on high surface area carbon. The concept is to exploit the high surface area and known favorable adsorbtion characteristics of carbon towards organics with the demonstrated visible photocatalytic oxidation of these organics by nanosize MoS_2. This might allow continuous regeneration of a "clean" carbon surface-eliminating the current necessity to dispose of contaminated carbon as occurs when all surface sites become occupied by pollutants.

It has also been convincingly shown recently (Tributsch, Science March 1998) that certain other metal sulfides are particularly resistent to oxidative degradation in bulk form-namely RuS2 and PtS2. Unfortunately, the bandgaps of these materials, like MoS_2, are too narrow to efficiently photooxidize organics. We expect that a synthesis of these materials in nanosize form will shift their bandgaps into the visible and make them possible photocatalyst candidates. We intend to synthesize them for the first time in nanosize form and test them singly and as hydrid combinations with nanosize MoS_2.

D.F. Kelley will be continuing his studies of electron and hole transfer using time-resolved PL and absorbance to better understand the chemical and structural features which influence high photocatalytic activity in nanosize MoS_2 and WS_2.