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PHOTOCATALYSIS USING SEMICONDUCTOR NANOCLUSTERS

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ABSTRACT

We report on experiments using nanosize MoS_2 to photo-oxidize organic pollutants in water using visible light as the energy source. We have demonstrated that we can vary the redox potentials and absorbance characteristics of these small semiconductors by adjusting their size, and our studies of the photooxidation of organic molecules have revealed that the rate of oxidation increases with increasing bandgap (i.e. more positive valence band and more negative conduction band potentials). Because these photocatalysis reactions can be performed with the nanoclusters fully dispersed and stable in solution, liquid chromatography can be used to determine both the intermediate reaction products and the state of the nanoclusters during the reaction. We have demonstrated that the MoS_2 nanoclusters remain unchanged during the photooxidation process by this technique. We also report on studies of MoS_2 nanoclusters deposited on TiO_2 powder.

INTRODUCTION

In addition to their large specific surface areas, nanoclusters often have unusual surface morphologies and bonding arrangements which can make them effective catalysts. We are interested in materials which are both photostable and absorb in the visible range to use as photo-oxidation catalysts to remove organic pollutants from aqueous systems. The concomitant photostability and absorbance requirements eliminate most previously investigated materials such as TiO_2 and CdS. Fortunately, through advances in the synthesis of nanocluster materials we have available several new materials including the photostable transition metal dichalcogenides such as MoS_2.

EXPERIMENT

Our nanoclusters are made by inverse micelle synthesis which results in nearly monodisperse, nanocrystalline clusters.[1,2] Surface modification in solution is used to purify and extract the clusters into a water-miscible solvent, acetonitrile and, following evaparation of this volatile solvent, the clusters are redissolved in water. Further purification of the nanoclusters using high pressure liquid chromatography (HPLC) and/or dialysis allows the nanoclusters to be characterized and used as catalysts.[3] We give three examples of photocatalysis using these dispersed clusters; the photo-oxidation of the organic pollutants phenol and pentachlorophenol (PCP) in water using nanoclusters of MoS_2 and an example of their use in organic solution for the oxidation of an alkyl chloride in acetonitrile. We have studied MoS_2 nanoclusters with light absorbance edges from 700 nm (d=8 nm) to 450 nm (d=3.0 nm) and have found that the optimum photo-oxidation performance for phenol oxidation occurs for a size of d~4.5 nm. These nanoclusters have an absorbance edge of ~550 nm, or a bandgap of ~2.2 eV (compared to the bulk MoS_2 value of 1.2 eV). For the other two examples, the optimal size appears to be d~3.0 nm.

We have recently reported on the photo-oxidation of phenol, and details of the experimental apparatus and chemical analysis technique(s) are described in ref [4]. In that work we reported that, when combined with TiO_2 as a support material, we could successfully oxidize phenol using only visible light (>450 nm) using d=8 nm MoS_2 with an absorbance onset of ~700 nm or d=4.5 nm clusters with an edge at 550 nm. For phenol oxidation using nanosize MoS_2 deposited on TiO_2 powder [4] we took advantage of charge carrier transfer between the nanoclusters of MoS_2 and the TiO_2 powder to increase the photo-oxidation capability of the latter material. It is also possible to modify MoS_2 nanoclusters by deposition of metals such as Pt and Ru but our experiments to date demonstrate such deposition *decreases* the photo-oxidation capacity of the semi-conductors.

DISCLAIMER

In recent work on the photo-oxidation of pentachlorophenol (PCP), described here for the first time, we have designed a custom photochemical reactor which has o-ring sealed access ports for introduction of controlled atmospheres and/or sampling of the liquid and/or gas phase(s) for analysis by HPLC or GC/MS. The former is used to quantitate the amount of PCP as a function of light exposure while the latter is used to identify the type of intermediate breakdown products of the photo-oxidation. The reactor is illuminated from above through a flat suprasil window by a collimated Xe arc lamp with a known spectral output. One or more optical filters are used to restrict the range of incident wavelengths. Typically we used a long-pass filter which only passes light with $\lambda>400$ and an IR short-pass filter which passes light with $\lambda<700$ nm. The photocatalyst with PCP in water is stirred rapidly by magnetic means. To determine the relative efficiencies of various nanocluster materials as photocatalysts we compare to the best available powder material, TiO_2 DeGussa P-25. We also use bulk CdS powder for experiments where $\lambda>400$ nm since TiO_2 has no light absorbance or catalytic activity under these conditions.

RESULTS

To illustrate the photo-oxidation process and our method of chemical analysis we show in Figure 1 an HPLC chromatogram taken with an in-line UV-visible detector. The chromatogram was obtained on a commerical HP 1040 HPLC system with three in-line detectors; a photo-diode array (PDA), a refractive index detector (RI), and a fluoresence detector (FL). The column used was a Hewlett-Packard, ODS-type, reverse phase c18 terminated silica column and the mobile phase was acetonitrile. We monitor the PDA detector output at the absorbance peaks of the organic molecule of interest. For example, in the case of PCP we monitor at 225 nm, 250 nm, and 325 nm, the principal absorbance peaks of PCP, to follow the destruction of this substance with irradiation time. In the case of the alkyl chloride of figure 1 we monitor at 250 nm. The RI detector can be used to detect non-absorbing chemicals. The FL allows sensitivites to aromatic molecules (e.g. phenol) in the ppb range without pre-concentration of the analyte, while the PDA array with a suitably chosen detection wavelength has sensitivities of 0.01 - 0.1 ppm. For the FL detector we excite at 250 nm and detect fluorescence at 320 nm. By calibration with a set of known organic standards and integration of the elution peak area(s) we obtain the concentration of the organic pollutant as a function of irradiation time.

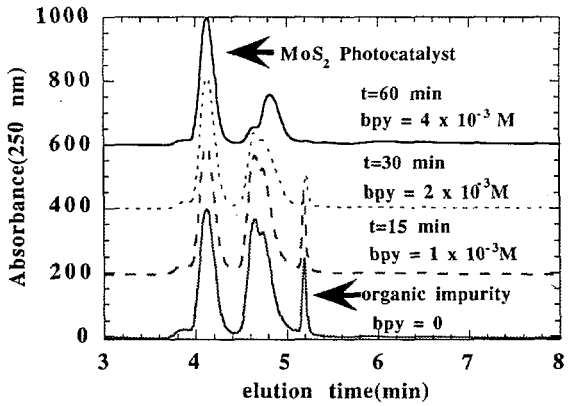

Figure 1. The photo-oxidation of an alkyl chloride impurity using room light illumination and d=3.0 nm MoS_2 dispersed nanoclusters is followed by HPLC using the 250 nm absorbance from a PDA detector.

In the data of figure 1 we show the photo-oxidation of an alkyl chloride using only fluorescent room lights and nanosize MoS_2 with d=3.0 nm. For solubility reasons, the experiment was performed in acetonitrile, a water miscible, chemically inert solvent. We use a sacrificial electon acceptor molecule, bipyridine, (bpy) to have a complete redox reaction. (In all other experiments in water the dissolved oxygen itself functions as an electron acceptor) Previous work has shown that the ability of bipyridine to accept photo-electrons from nanosize MoS_2 depends on

the nanocluster size, being most rapid for the smallest d=3.0 nm clusters with the widest bandgap.[5] We have previously shown by time-resolved fluoresence that the rate of electron transfer (E.T.) for a fixed size cluster depends on the redox potential of the substrate organic molecule-as expected, more difficult-to-reduce molecules slow down the E.T. process. In the present reaction too, we found the kinetics to be most rapid with the d=3.0 nm clusters despite the fact that these clusters only begin absorbing light at around 450 nm. Furthermore, the most easily oxidized organic (the alkyl chloide) disappears first, followed by the other organic contaminants (eluting between 4.5 and 5 minutes in the above figure).

In the experiment of figure 1, the alkyl chloride which is identified as eluting in t=5.18 minutes in figure 1, is oxidized by the MoS_2 holes which are created using only visible room lights. This reaction at the nanocluster concentration of only ~0.1 mg/ml MoS_2 is remarkably rapid, completely eliminating this impurity in less than 1 hr. All other organic impurities, eluting inear t=4.7 minutes in figure 1 disappear after about 3 hrs. We determine the MoS_2 concentration in the purfied nanoclusters in water by x-ray fluoresence spectroscopy (XRF) vs. known Mo standards. By this method we have found the Mo:S atomic ratio to be ~1:2.5, showing the presence of excess sulfur, probably on the surface of the clusters. Other organic impurities, also separated and observed in the chromatogram of figure 1, but not identified by GC/MS, are later oxidized by the nanoclusters after the alkyl chloride is destroyed.

Under our chromatography conditions, the nanosize MoS_2 clusters elute completely from the column and are separated from the organic components of the mixture. The peak eluting at t=4.1 minutes can be identified as the clusters from the complete absorbance profile obtained by the PDA during the run. The structured absorbance profile of the t=4.1 min elution peak is shown before and after complete oxidation of all the organics in figure 2 and is characteristic of monodisperse nanocrystalline semiconductors. Its electronic features and their relationship to the bulk has been elucidated previously.[6] An important aspect of being able to separate the inorganic nanosize photocatalyst from the chemical reactants and products is the ability to acertain that no chemical changes or degradation of the nanoclusters occurs during the reaction (i.e. it functions as a true catalyst). This has not been possible with previous work involving slurries of aggregated powders-but is a critical issue.

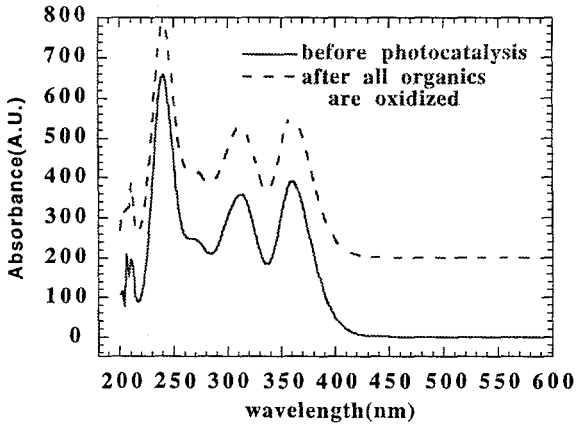

Figure 2. The absorbance profile of the MoS_2 nanocluster peak eluting at t=4.1 minutes in figure 1, is shown before and after all organics are photo-oxidized.

Using the methodology outlined above one can also study the photo-oxidation of phenol in water using only nanosize MoS_2 and visible light. In this case no sacrificial electron acceptor is required. In this experiment the light was supplied by a 200 W Xe arc lamp with a long pass filter which allows only light >450 nm to irradiate the photochemical reactor. Figure 3 shows the phenol concentration as a function of time under these very demanding conditions compared to performing the same oxidation using Degussa P-25 (the most active photocatalyst currently available) at the concentration of 1 mg/ml. Keeping in mind the low concentration of 0.1 mg/ml of nanoclusters in solution this degradation of phenol is impressive. We found that only the d=4.5 nm clusters with an absorbance edge near 550 nm were able to degrade the phenol under these

irradiation conditions, while the d=8.0 nm clusters didn't have a positive enough valance band potential (because of reduced quantum confinement effects).

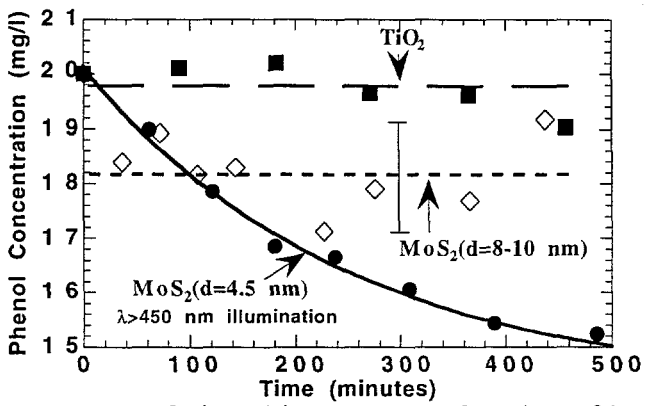

Figure 3. Rate of disappearance of phenol in water as a function of irradiation time using a Xe lamp with a 450 nm long-pass filter for three photo-catalysts.

It is also possible to combine nanosize MoS_2 with other semiconductors such as TiO_2 to improve the combined photo-oxidation activity. As an example of this synergism consider figure 4 where a very small deposition of MoS_2 clusters onto TiO_2 has a significant improvement on its activity. Here we illuminated at 360 nm with a 10 W spectraline lamp to take advantage of both the MoS_2 and TiO_2 absorbances. It is interesting to note in this figure that addition of too large an amount of MoS_2 actually reduced the TiO_2 activity, perhaps by blocking key phenol binding sites on the TiO_2 lattice. The idea of achieving improved photo-charge separation by combining two semiconductors with different band gaps may be applicable to nanosize semiconductors deposited onto bulk materials such as Degussa TiO_2, just as it is used in solar voltaic devices. We feel that improvements in the physical contact between the two semiconductors may substantially improve on the results of figure 4. In these initial experiments, the nanoclusters were simply deposited by precipitation from solution onto the TiO_2 powder with no subsequent thermal treatment to improve chemical interaction between the materials. Since the ability to transfer charge between lattice sites depends exponentially on the spatial distance between them, increased bonding by thermal treatment may further improve on the results of figure 4. Experiments to this end are currently in progress.

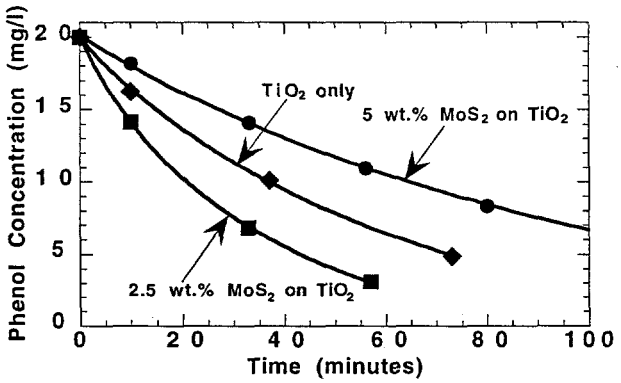

Figure 4. The rate of disappearance of phenol in water as a function of loading of nanosize MoS_2 is shown vs. irradiance time.

Many of the typical pollutants found in aqueous environments are chlorinated aromatics. A typical example is pentachlorophenol, (PCP), a wood preservative. This robust molecule is very long-lived under normal sunlight conditions as it has no absorbance above 350 nm, so we were interested in studying its photo-oxidation using only visible light and our nanosize MoS_2 clusters.

An experimental difficulty arises when comparing our new inorganic nanoclusters to typical photocatalysts such as TiO_2 since we don't expect nor observe any photo-oxidation activity if a

long-pass, 400 nm filter is used with our Xe arc lamp to mimic the solar spectrum. So we make a comparison of our nanoclusters to a visible light absorbing material, CdS, in the form of a macroscopic powder slurry. CdS begins absorbing at around 530 nm so its absorbance characteristics are quite similar to those of our d=4.5 nm MoS_2 clusters. Of course, it would never be practical to use CdS as a photo-oxidation catalyst because of toxicity concerns due to Cd ion release upon photodegradation!

Figure 5 shows the observed photo-oxidation kinetics of PCP obtained by monitoring the absorbance of the 250 nm absorbance peak of PCP using our PDA detector. A control with no catalyst, a CdS powder slurry at 0.1 mg/ml, and two different sized MoS_2 nanocluster dispersions are shown in this figure. We also monitor the absorbance peaks of PCP at 225 and 325 nm, but because of the presence of chlorine on the aromatic ring are unable to utilize the very sensitive FL detector as we did in the phenol oxidation experiments (i.e. the fluoresence is quenched by the chlorine). Never the less, we can monitor the PCP abundance starting at the initial concentration of 10 ppm (near its solubility limit in water) to approximately 0.01 ppm, with no special pre-concentration methods. As can be observed in this figure, no photo-oxidation takes place with no catalyst (or with Degussa TiO2 for that matter, not shown), while CdS has some photo-oxidation ability. Both samples of MoS_2, though at lower concentrations than the CdS, have a sigificantly improved photo-oxidation capability. (The concentration of the nanosize MoS_2 in the water was obtained directly by XRF)

It is important to note that intermediate, aromatic photooxidation products of the break-down of PCP are observed for all the catalysts shown in figure 5 within the time scale shown. However, these intermediates are themselves photooxidized completely to CO_2 and HCl on a reasonable time scale (i.e. < 1 day) and a pristine HPLC chromatogram showing only the nanosize MoS_2 is observed as in figure 1. A longer paper addressing these details will be published.

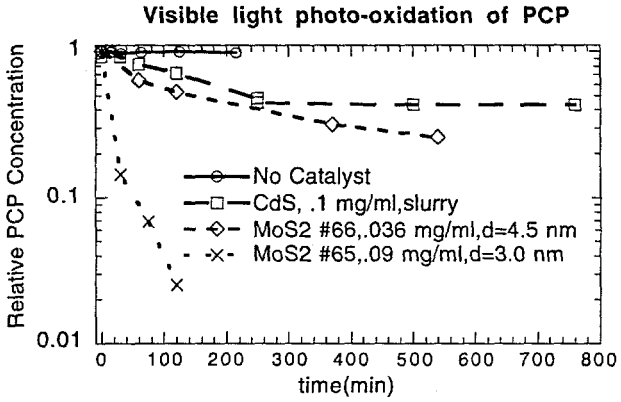

Figure 5. The rate of photo-oxidation of PCP is shown as function of visible light irradiation time for four conditions. The plot is semi-logrithmic.

CONCLUSIONS

In photo-oxidation experiments with an alkyl chloride the smallest d=3.0 nm MoS_2 nanoclusters have the fastest rate of organic destruction though they absorb less of the available spectrum than larger MoS_2 nanoclusters. Further, we showed that even when restricting the light irradiance to >450 nm, a significant rate of phenol photo-oxidation could be achieved with nanosize MoS_2 with a size of d=4.5 nm and an absorbance onset of ~550 nm. In PCP photo-oxidation studies we demonstrated that d=3.0 nm MoS_2 nanoclusters irradiated only with the visible light output of a Xe arc lamp photo-oxidize PCP faster than the best available UV photo-oxidation catalyst Degussa P-25 TiO_2 using the entire UV and visible light output from the same lamp!

ACKNOWLEDGMENTS

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