1st Int. Cong. on Environmentally Conscious Manufacturing, 9/18-20/91
Santa Fe, NM

Conf-9109259--12
SAND--91-2164C
DE92 002363

ENHANCING SOLAR PHOTOCATALYTIC DETOXIFICATION BY ADSORPTION OF PORPHYRINS ONTO TiO_2

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ABSTRACT

Titanium dioxide (TiO_2) is a known photocatalyst for solar detoxification of water containing organic contaminants including PCB's and dioxins. Unfortunately, the UV light used by the photocatalyst only comprises about 4% of the solar spectrum. Metalloporphyrins strongly absorb in the visible and near infrared region. Using visible light, we have investigated Ni(II) uroporphyrin (NiUroP), Sn(IV)Cl_2 uroporphyrin (SnUroP) and Sn(IV)Cl_2 tetrakis(p-carboxyphenyl)porphyrin (SnTCPP) as possible enhancers of destruction of a model organic compound, salicylic acid (SA), by means of photosensitization of colloidal TiO_2 particles. All three porphyrins are found to adsorb reversibly onto the colloidal TiO_2 upon variation of pH. Adsorption of porphyrins results in the increased colloidal stability of fine TiO_2 particles in the pH range 5-8. While NiUroP on TiO_2 does not show any enhancement of photodestruction, the adsorption of SnUroP increases the destruction rate compared to that of the bare TiO_2 surface. The effect of ambient oxygen on the observed photolability of the Sn porphyrins and enhancement of photodestruction of SA was also investigated. SnTCPP does not photodecompose upon illumination either in the presence or absence of TiO_2, but neither does it bind to the photocatalyst at pH 6. At pH 4.5 it adsorbs onto TiO_2 but it also photodecomposes at this pH. We are attempting to stabilize the adsorbed porphyrins by adding suitable peripheral substituents onto the porphyrin macrocycle.

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INTRODUCTION

Toxic waste disposal represents a major problem of international importance. There is a clear and present need to develop and characterize fundamental chemical processes that can be used to detoxify various classes of toxic chemical wastes. In particular, polyhalogenated hydrocarbons present a major challenge. To illustrate, polychlorinated biphenyls (PCBs) are highly toxic carcinogens and mutagens even at low concentrations.[1-6] Moreover, conventional methods for destruction (incineration) require high concentration of PCBs and appear to produce dioxins.

Solar photocatalytic detoxification of water provides an attractive new approach to treatment of waste contaminated water.[7-15] In this process, sunlight is focused onto a reactor through which the contaminated water is flowing. Ultraviolet energy in the concentrated beam activates a catalyst (titanium dioxide) in the waste stream. Activated sites on the catalyst surface react with dissolved oxygen or added oxidants, causing formation of reactive radicals, which in turn attack the organic waste components. There are generally no hazardous products formed. The process is capable of destroying most halogenated and non-halogenated organic compounds including solvents, PCBs, dioxins, pesticides, and dyes.[7-15] Unfortunately, the energy used by TiO_2 only constitutes about 4% of the solar spectrum.[16] It would be advantageous to use all of the solar energy to drive a TiO_2 photocatalytic waste detoxification process.

One way of enhancing the efficiency of solar detoxification technologies is to utilize a larger portion of the solar spectrum to initiate detoxification chemistry. This can be accomplished by adsorption of appropriate dye molecules onto TiO_2. The dye absorbs visible light not utilized by bare TiO_2, initiating photochemical redox reactions by electron transfer with the TiO_2 surface.[17-21] Metalloporphyrins are chemically robust dyes with strong absorption bands throughout the visible spectrum. Moreover, porphyrins with carboxylic acid peripheral substituents are known to adsorb onto the TiO_2 surface.[17,18,22] The longer term goals of this work are to design and develop new sensitizers that will increase the efficiency and stability of photocatalytic systems.

PROCEDURES AND RESULTS

Coupling of Existing Solar Collector Technologies and Sensitized-Photocatalysts. Using both trough and heliostat systems, workers at Sandia National Laboratories (SNL) have successfully destroyed low concentrations of a model organic compound, salicylic acid (SA), by using semiconductor substrates alone. Although SA is not a real contaminant, it has destruction rates similar to waste contaminants.[15] A parabolic trough collector with a glass pipe reactor and heliostat with a falling-film reactor were used in the tests.

In order to expand the efficiency of the TiO_2 substrates in the visible region of the spectrum, work is now well underway to adsorb various MPs onto TiO_2 substrates. Among different classes of visible light absorbing dyes that one can choose to sensitize photochemical reactions on large bandgap semiconductors, the porphyrins stand unique.[7-18] Figure 1 illustrates a proposed charge-induction mechanism for ZnUroP on the TiO_2 surface. Electrons injected into the conduction band can be trapped by dissolved O_2 to form superoxide ion.[15] It has been suggested that hydrogen peroxide is formed from superoxide. Thus, sensitizing TiO_2 may result in photoproduction of hydrogen peroxide, mitigating the need of H_2O_2 addition to the waste stream.

We have extended this preliminary work to include several classes of water soluble metalloporphyrins (MPs) whose structures are shown in Figure 2. Our initial efforts in this regard have concentrated on characterizing the solution/adsorption behavior of commercially available MP sensitizers adsorbed onto TiO_2 colloidal suspensions, and the quantification of the net photocatalytic behavior of these systems.

Preparation of Metalloporphyrin Sensitized TiO_2 Substrates. The photosensitized samples were prepared by adding solid TiO_2 and salicylic acid (SA) to a tin-porphyrin (SnP) solution for a final composition of ~15 µM SnP/0.1% TiO_2/30 ppm SA. Components were added in different orders and varying compositions to determine the effect of competitive adsorption processes on the TiO_2 surface. The amount of porphyrin adsorbed onto the TiO_2 surface was measured by following the decrease in the Soret band absorption (~400nm) of the MP as a function of pH. A UV filter was placed between the mercury vapor lamp and the sample solution in order to use only the visible portion of the lamp spectrum, >390 nm unless otherwise indicated. The dispersion of small TiO_2 particles depends on pH and is influenced by the presence of the MP (see below). When these fine

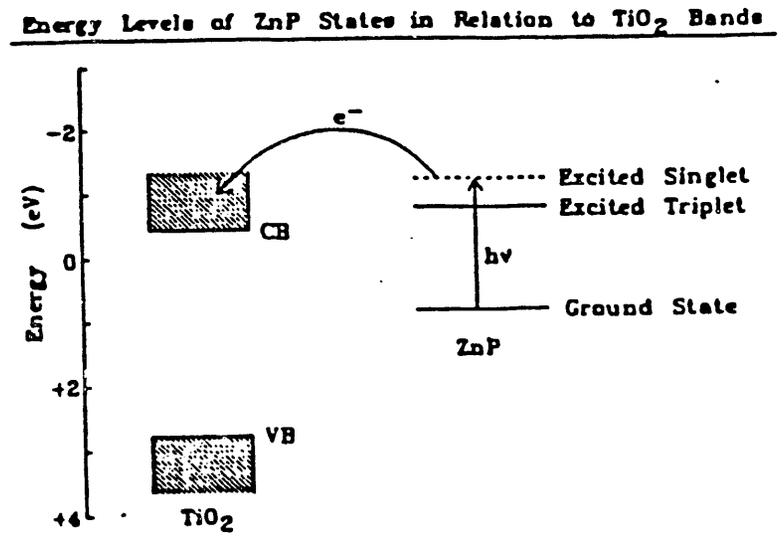

Figure 1. Visible light photosensitization to TiO2 by metalloporphyrin.

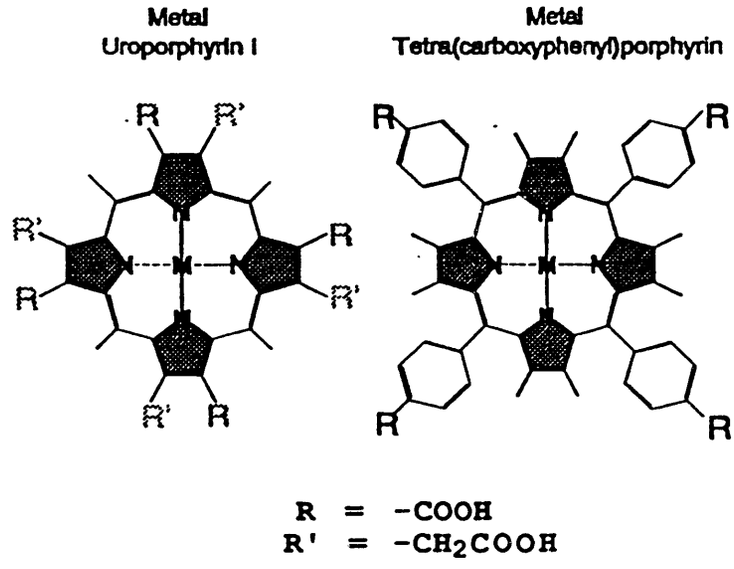

Figure 2. Schematic representation of metalloporphyrin structures.

particles appear in solution a broad, flat UV absorption band is observed in the range from 200-340 nm. The concentration of the particles is quantified by the absorbance at 296 nm.

Our data conclusively show that the presence of a MP sensitizer dramatically affects the solution behavior of suspended TiO_2 colloids. In the absence of MP, solvation of fine TiO_2 particles occurs only at high (>9) and low (<5) pH, but not in the pH range from 5 to 8. This is illustrated in Figure 3, where the absorbance due to the conduction band of the fine particles at 296 nm is plotted versus pH. The conduction band absorption is relatively flat at wavelengths less than 300 nm, so the absorption at 296 nm was used to quantify the concentration of solvated TiO_2.

The presence of SnUroP shifts the range in which dispersion occurs to above pH 5. The pK of the acid substituents of uroporphyrin is about 6.6,[23] the pH at which SnUroP starts to adsorb onto the surface. This suggests that tin uroporphyrin interacts dynamically with the surface in the pH range from 5 to 8, and the interaction results in the dispersion of TiO_2. Binding of porphyrin evidently neutralizes the charged regions, preventing electrostatic repulsion that might break up aggregates of small TiO_2 particles. SnTCPP does not appear to influence the dispersion process as strongly, although enhanced solvation may occur in the region where bare TiO_2 is not dispersed. The presence of salicylic acid does not appear to influence the solvation of TiO_2.

As a first step in developing a stable photosensitized TiO_2 catalyst, we compared the chemical effects of adsorption of two SnPs onto the TiO_2. Adsorption of SnUroP was converted the porphyrin to a reduced porphyrin species. UV-visible spectra obtained before and after the adsorption of porphyrin clearly show the formation of the Sn urochlorin.[24] In contrast, simply adsorbing SnTCPP onto the TiO_2 surface at pH 4.5 does not result in conversion of the porphyrin to a reduction product.

Initial Studies of Photocatalytic Activity of tin(IV) Porphyrins and Their Photosensitization Effect on TiO_2. Our primary goal is to enhance TiO_2 redox reactions that destroys salicylic acid, by using the visible light absorbed by a photosensitizer. For the photosensitized TiO_2, absorption of visible light by the MP results in the formation of excited triplet states. The redox potentials of the MP are altered in the excited state, and these new species are then available either (1) to interact with electrons and/or holes of TiO_2, (2) to add species with different redox properties that can

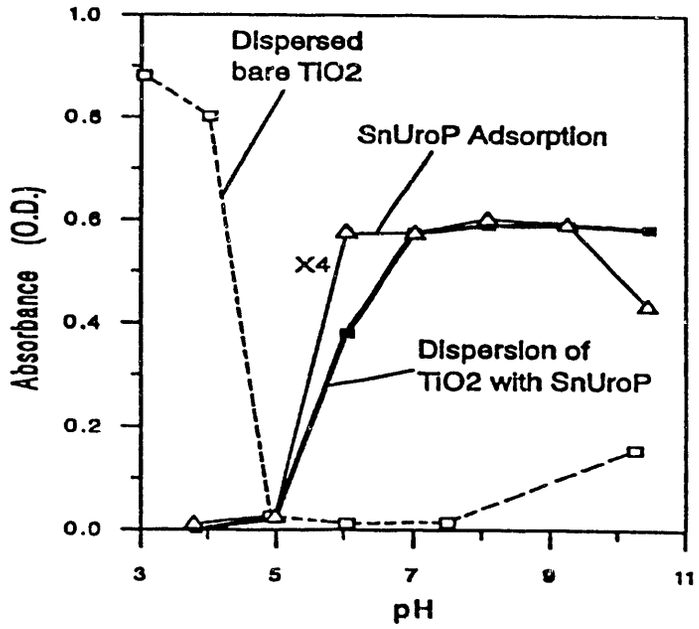

Figure 3. pH dependence of the dispersion of small TiO_2 particles for bare TiO_2 and for TiO2 photosensitized with SnUroP (measured by the conduction band absorbance at 296 nm), and the adsorption of SnUroP onto TiO_2 (measured by the Soret band absorbance at 402 nm of the SnUroP remaining in solution).

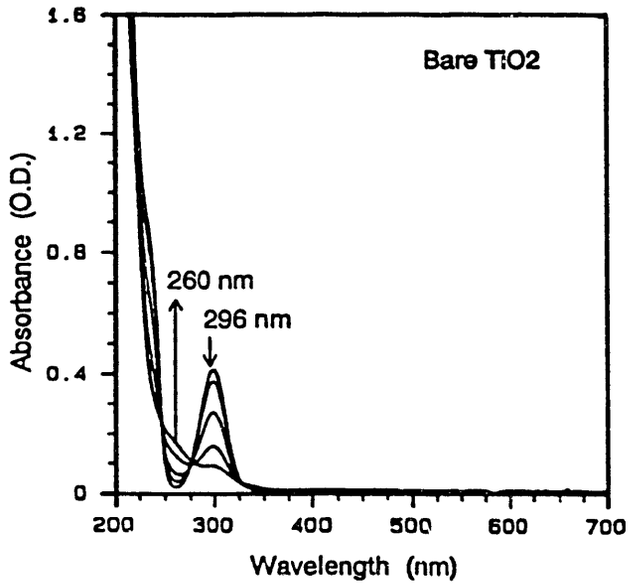

Figure 4. Change in the absorption spectrum upon irradiation of an aqueous mixture of colloidal TiO_2 and salicylic acid at pH 5 (SA/TiO_2). Spectra are taken at 0, 5, 20, 40, and 60 minutes.

modify rates of destructive reaction pathways, or (3) to participate directly in detoxification redox reactions with SA.

In the absence of TiO_2, both Sn porphyrins show photoactivity for the conversion, but not destruction of salicylic acid. Photocatalytic conversion of salicylic acid is indicated by the increase in absorbance between the SA absorption peaks at 230 and 296 nm, and other changes in the SA absorption spectrum. The conversion product is thought to be a slightly modified aromatic ring compound. Tin(IV)Cl_2 uroporphyrin (SnUroP) photodecomposes considerably during 90 minutes irradiation with visible light. The reduction product is mostly the Sn-urochlorin [24] in which the b-carbons of one pyrrole ring of the porphyrin are reduced and urophlorins [24] may also be formed. Tin(IV)Cl_2 tetrakis(p-carboxyphenyl)porphyrin (SnTCPP) does not photodecompose in the absence of TiO_2.

Visible-light assisted reactions occurring in a solution containing SA and the porphyrin-sensitized TiO_2 were monitored as a function of irradiation time to determine if the destruction of SA was enhanced by the presence of the metalloporphyrin dye. UV-visible spectra of samples taken at various irradiation times for unsensitized (bare TiO_2) and dye-sensitized systems are shown in Figures 4 and 5, respectively.

For the SA/TiO_2 mixture, enough absorption into the edge of the conduction band occurs to generate electron-hole pairs so that the destruction of the SA occurs, but at a much slower rate than that with UV irradiation of the solution. Also the rise in absorbance to the red of the 296-nm SA peak and in the valley (at about 260 nm) between the 296- and 230-nm peak shows evidence of the formation of a degradation product of SA.

In the presence of SnUroP adsorbed onto TiO_2, the destruction of SA results in more complicated spectral bahavior. A much larger rise than that observed in the absence of SnUroP in the UV absorbance below 350 nm is observed and presumably results from the formation of a much greater concentration of the intermediate SA product. We speculate that the intermediate is similar to the intermediate formed at a much lower level in the absence of the porphyrin. Solvation phenomenon may also play a role in increasing the UV absorbance. Using the absorption spectra, we can estimate and compare the rates of destruction of SA. The absorbance at the peak of the SA band at 296 nm, a measure of the conversion and destruction of SA, is plotted in Figure 6 as a function of irradiation time for photosensitized TiO_2 (TiO_2/SnUroP) and bare TiO_2. An enhanced rate of

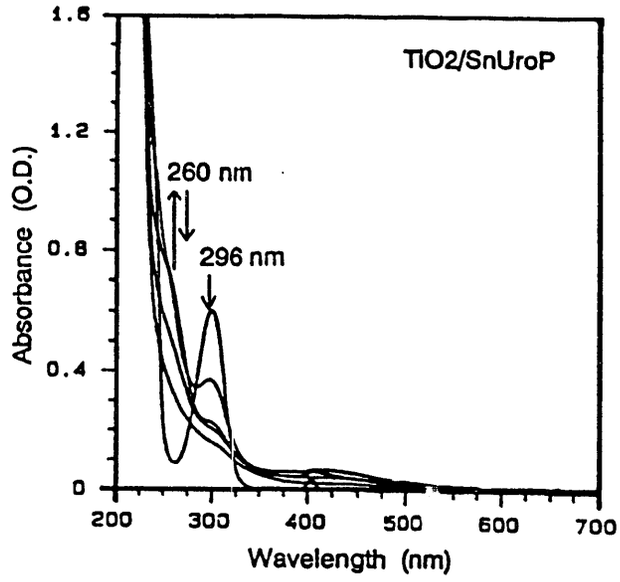

Figure 5. Change in the absorption upon irradiation of an aqueous mixture of tin-uroporphyrin-modified colloidal TiO_2 and salicylic acid at pH 5 ($SA/TiO_2/SnUroP$). Spectra are taken at 0, 5, 20, 40, and 60 minutes.

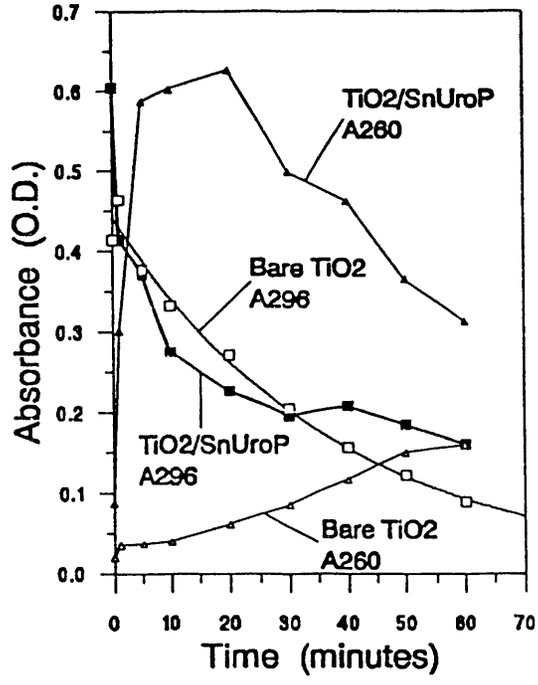

Figure 6. Enhancement of salicylic acid detoxification using Sn uroporphyrin as a photosensitizer. Salicylic acid absorbance at 296 and 260 nm (1-cm cell) is plotted against irradiation time. The curve through the data points for bare TiO_2 at 296 nm is an exponential fit.

salicylic acid destruction is observed in the presence of adsorbed SnUroP on the TiO_2 surface when compared to that of bare TiO_2. The enhancement in the detoxification rate is most apparent in the slope of the curve for the photosensitized TiO_2 within 30 minutes of illumination. The pseudo-exponential rate in the first 20 minutes is about 2 5 times faster than the exponential destruction rate for bare TiO_2. The SA peak at 230 nm evolves in a similar way with illumination time. This indicates a strong increase in the rate of formation of the initial SA product and then its further destruction at a rate consistent with bare TiO_2.

MECHANISMS FOR ENHANCED PHOTODETOXOFICATION

Characterizing the mechanism(s) of photodetoxification is vital for the production of improved photocatalytic systems. A number of mechanisms could lead to enhancement of photocatalytic activity. First, the absorption of visible light by the porphyrin could lead to a redox cycle that generates reactive porphyrin species (e.g., the anion and/or cation) that directly attack salicylic acid. Evidence for such a process is found in the rapid conversion of SA to some species, regardless of whether TiO_2 is present. Enhancement would occur if the SA product is more labile. A second mechanism of photosensitization involves the removal of conduction band electrons by reduction of the porphyrin triplet state at +1.1 V versus NHE. Removal of electrons from TiO_2 would prevent rapid electron-hole recombination, leaving the strongly oxidizing hole for reaction with adsorbed SA. This is equivalent to the enhancement observed when metal ions and other additives are used to extract conduction band electrons from TiO_2.[25] This mechanism would be consistent with the production of reduced porphyrin products. Reduction of Sn porphyrins is known to result in a long-lived radical anion (at -0.66 V for SnUroP) that eventually decomposes unless it is re-oxidized soon to the neutral porphyrin. Indeed, inclusion of methylviologen, an electron acceptor (-0.45 V) does seem to protect the porphyrin from degradation beyond the Sn chlorin. The potential of the Sn porphyrin anion is sufficient for H_2 generation. Alternatively, reduction of the porphyrin triplet by solution species would result in the anion which could inject electrons into the conduction band. Enhancement mechanisms involving porphyrin oxidation chemistry via the oxidation of either the triplet state at -0.13 V or the neutral porphyrin at >1.64 V by valence band holes also cannot be ruled out. Most likely either oxidative or reductive reactions of the porphyrin initiate the destruction of the porphyrin. Determination of the

mechanism of porphyrin degradation on TiO_2 will allow us to design more stable photosensitizers.

When photosensitization experiments are repeated in the absence of O_2 (under a nitrogen atmosphere), almost no change in the salicylic acid spectrum is observed. This suggests that O_2 is required for both destruction of salicylic acid and formation of the SA intermediate species. SnUroP photosensitizes the formation of singlet O_2 with high quantum yield (~0.6),[26,27] and singlet oxygen could be involved in forming the SA intermediate. However, for the bare TiO_2 surface also, oxygen is required for the destruction of salicylic acid, and this requirement is maintained in the presence of the photosensitizer.

SUMMARY

The properties of two tin porphyrins were investigated with regard to their ability to enhance the destruction rate of salicylic acid by TiO_2. Adsorption onto TiO_2 occurs below the point of zero charge of the TiO_2 surface, and for SnUroP results in reduction of the porphyrin macrocycle. Interaction of the porphyrins with the surface modifies the colloidal properties of TiO_2. Sn-porphyrin-modified TiO_2 shows enhanced ability to photocatalytically destroy salicylic acid. The complete mechanism of enhancement remains to be determined. The destruction efficiency also remains to be improved for the commercial viability.

SnUroP itself is rapidly destroyed during the detoxification reaction. SnTCPP shows greater stability on the TiO_2 surface, but is apparently also ultimately destroyed. We are attempting to stabilize the adsorbed porphyrins by adding suitable peripheral substituents onto the porphyrin macrocycle in order to either change their interactions with the surface or modify their electronic properties.

ACKNOWLEDGEMENTS

This work is supported by a grant from DOE/NMSU Waste Management Education & Research Consortium (to MRO) and the U.S. Department of Energy Contract DE-AC04-76DP00789 (to MRP).

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