

ENHANCEMENT OF SOLAR PHOTOCATALYTIC DETOXIFICATION BY ADSORPTION OF PORPHYRINS ONTO TiO₂*

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ABSTRACT

Titanium dioxide (TiO₂) is a photocatalyst for solar detoxification of water containing organic contaminants such as solvents, PCB's, dioxins, pesticides, and dyes. Unfortunately, the ultraviolet (UV) energy used by TiO₂ ($\lambda < 400$ nm) only comprises about 4% of the solar spectrum. One way of enhancing the efficiency of solar detoxification technologies is to utilize a larger portion of the solar spectrum to initiate the TiO₂-catalyzed detoxification chemistry. Metalloporphyrins strongly absorb visible and near infrared radiation. By utilization of a process called photosensitization, adsorption of these dyes onto TiO₂ can enable a much broader portion of the solar spectrum to be used. Photosensitization relies upon the ability of the dye molecule to absorb more of the solar energy than bare TiO₂ and to interact electronically with the TiO₂ surface in such a way as to initiate TiO₂-based redox photochemistry using the dye-absorbed energy.

Using visible light, we have investigated Ni(II) uroporphyrin (NiUroP), Sn(IV)Cl₂ uroporphyrin (SnUroP) and Sn(IV)Cl₂ tetrakis(*p*-carboxyphenyl)porphyrin (SnTCPP) as possible enhancers of destruction of a model organic toxic compound, salicylic acid (SA), by means of photosensitization of colloidal TiO₂ particles. All three porphyrins are found to adsorb reversibly onto the colloidal suspension of TiO₂ powder upon variation of pH. Adsorption of these porphyrins results in the induced colloidal stability of fine TiO₂ particles in a pH range where the colloid is not normally formed. While NiUroP on TiO₂ does not show any enhancement of photodestruction of salicylic acid, the adsorption of SnUroP increases the destruction rate compared to that of the bare TiO₂ surface. The enhancement of destruction is presumably due either (1) to injection of electrons from the reduced Sn porphyrins into the conduction band of TiO₂, (2) to reduction of porphyrin by conduction band electrons, or (3) to photosensitization involving the production of reactive species such as singlet O₂. The effect of ambient oxygen on the observed photolability of the Sn porphyrins and the contribution of oxygen species to enhancement of photodetoxification was investigated. SnTCPP does not photodecompose upon illumination either in the presence or absence of TiO₂, but neither does it bind to the TiO₂ surface at pH 6. At pH 4.5, SnTCPP is fully adsorbed onto TiO₂ but it also photodecomposes at this pH. We are trying to stabilize photodegradable porphyrins, such as SnUroP, by modifying them with suitable substituent groups at the periphery of the porphyrin moiety.

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Introduction

Toxic waste disposal represents a major problem of international importance. There is a clear and present need to develop chemical processes that can be used to detoxify various classes of toxic chemical wastes. For example, polyhalogenated hydrocarbons, benzene, and sulfur compounds present a major challenge. In particular, polychlorinated biphenyls (PCB's) are known to be highly toxic carcinogens and mutagens even at low concentrations.¹⁻³

Titanium dioxide (TiO_2) is capable of using UV light for the photocatalytic detoxification of aqueous, organic waste contaminants, including solvents, PCB's, dioxins, pesticides, and dyes.⁴⁻⁶ For many reasons, it would be advantageous to use direct solar energy to drive a TiO_2 photocatalytic waste detoxification process. In general, the toxic compound is oxidized to harmless compounds like dilute acids, water, and CO_2 , and no hazardous products are formed. Unfortunately, the energy used by TiO_2 , ($\lambda < 400\text{nm}$), only comprises about 4% of the solar spectrum (see Figure 1).⁷

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 and thereby improving the utilization of the available solar energy to drive the detoxification process.⁸⁻¹⁰

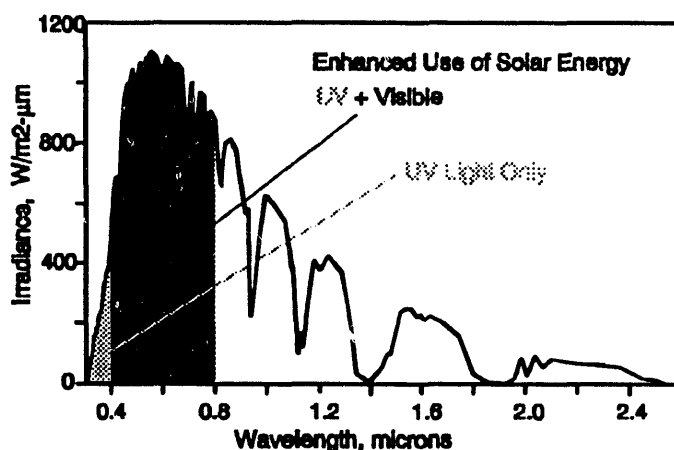


Figure 1. Direct Normal Solar Spectrum (Air Mass 1.5). Shaded region (light and dark) shows portion of solar spectrum used by photosensitized TiO_2 catalysts. Only the ultraviolet (light shaded region) is used by bare TiO_2 .

Metal porphyrins and metal phthalocyanines are chemically robust dyes with strong absorption bands throughout the visible portion of the electromagnetic spectrum. Moreover, porphyrins with carboxylic acid peripheral substituents are known to adsorb readily to the TiO_2 surface.^{8,9} Consequently, we have investigated the ability of Ni(II) uroporphyrin (NiUroP), Sn(IV)Cl₂ uroporphyrin (SnUroP) and Sn(IV)Cl₂ tetrakis (p-carboxyphenyl) porphyrin (SnTCPP) to enhance destruction of a model organic compound, salicylic acid, through the photosensitization of colloidal TiO_2 particles. The structures of these metalloporphyrins are shown in Figure 2.

The main objective of this work is to demonstrate that attachment of suitable and stable porphyrins to the TiO_2 semiconductor surface provides more efficient electron transfer between the photosensitizer and TiO_2 and thereby enhances solar photocatalytic detoxification. A second objective is to develop an understanding of the mechanism of porphyrin dye-enhanced solar detoxification. A third goal of this work is to stabilize the photodegradable photosensitizers on the TiO_2 surface to obtain the optimal photosensitization over a long period of time.

Materials and Methods

The TiO₂ powder used in this study was obtained from Degussa (P-25) or from Tioxide. P-25 TiO₂ contains a mixture of 80% anatase (band gap, 3.2 eV) and 20% rutile (band gap, 3.0 eV), whereas Tioxide TiO₂ contains almost entirely the anatase form. The surface area of the Tioxide TiO₂ (268 m²/g) is also about five times as great as for P-25. Both semiconductor materials have large particle size distributions. The uroporphyrins were obtained from Porphyrin Products and SnTCPP was obtained from Mid Century Chemical. All porphyrins were used without further purification. Reagent grade salicylic acid was purchased from Fisher Scientific. The water used was deionized with a conductivity of ~1 μmho.

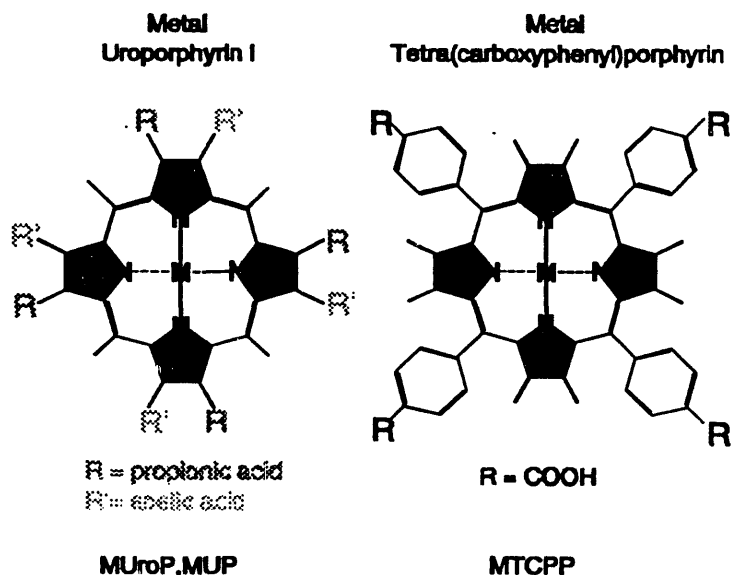


Figure 2. Porphyrins Used As Photosensitizers ($M=Sn$).

The photosensitized samples were prepared by adding solid TiO₂ and salicylic acid (SA) to a tin-porphyrin (SnP) solution for a final composition of ~15 μM SnP, 0.1% TiO₂, and 30 ppm SA (pH 6.0). The mixture gives a cloudy, white dispersion in the absence of porphyrin, but, in the presence of porphyrin, gives either a cloudy, pink (high pH) or a cloudy, green (low pH) mixture. Without stirring much of the TiO₂ settles out. Components were added in different orders and in varying compositions to determine the effect of competitive adsorption onto the TiO₂ surface. The amount of porphyrin adsorbed onto the TiO₂ surface was measured by following the decrease in the Soret band absorption (~400 nm) of the porphyrin while the pH of the solution was adjusted to the operating pH (4.5, 5.0, or 6.0).

A UV filter was placed between a mercury vapor lamp and the sample mixture to use only the visible portion of the lamp spectrum, $\lambda > 390$ nm unless indicated otherwise. Samples were collected at regular intervals up to 240 minutes for immediate analysis using a HP8452A UV-visible absorption spectro-photometer. All of the samples were either centrifuged for 20 minutes at 3400 rpm or centrifuged and filtered through 200-nm filters before recording the UV-visible spectrum of the transparent supernatant solution.

Before performing the experiments under visible light, some of the TiO₂ samples were washed with water (pH 6.0) several times in an effort to remove the colloidal TiO₂ stabilized by the presence of porphyrin. The colloidal dispersion of small TiO₂ particles depends on pH and is influenced by the presence or absence of porphyrin (see below). When these fine particles appear in solution a broad, flat UV absorption band is observed in the range from 200-340 nm (see Figure 3) and the concentration of the particles is quantified by the absorbance at 296 nm, also a peak position of salicylic acid when present. In some cases the porphyrin-stabilized dispersion of TiO₂ was removed by repeated washing of TiO₂ with water at pH 6.0.

Results and Discussion

Photocatalytic activity of tin(IV) porphyrins. In the absence of TiO_2 , both Sn porphyrins in solution show photoactivity for the conversion, but not destruction of salicylic acid. Photocatalytic conversion of salicylic acid is indicated by the increase in absorbance near 260 nm between the SA absorption peaks at 230 and 296 nm, the increase in absorbance in the wings on the red side of the 296-nm absorption band, and other changes in the SA absorption spectrum. The conversion product is thought to be a slightly modified aromatic ring compound that is yet to be identified. SnUroP photodecomposes considerably during 90 minutes irradiation with visible light. The initial pink color changes to green; from the absorption spectrum of the green pigment, the reduction product is mostly the Sn-urochlorin¹¹ in which the β -carbons of one pyrrole ring of the porphyrin are reduced and urophlorins¹¹ may also be formed. SnTCPP does not photodecompose in the absence of TiO_2 .

Photosensitization of TiO_2 . By combining either of these two porphyrins with TiO_2 yields a colored TiO_2 powder due to the absorption of visible light by the adsorbed Sn porphyrin on the colloidal TiO_2 particles. Binding to the surface occurs at lower pH for SnTCPP (pH 4.5) than for SnUroP (pH 6.0). The attachment of SnUroP to the semiconductor surface enhances the destruction rate of SA as described below (see Figure 7). Determination of the degree of enhancement is complicated by the generation of a salicylic acid intermediate product (see below) and, in the pH range above 5, by the dispersion of small TiO_2 particles. The complication in the analysis arises because both processes result in an increase in the absorbance in the UV portion of the absorption spectrum, interfering with the SA band at 296 nm used to monitor its destruction. The UV absorption that is caused by fine TiO_2 dispersions is shown in Figure 3.

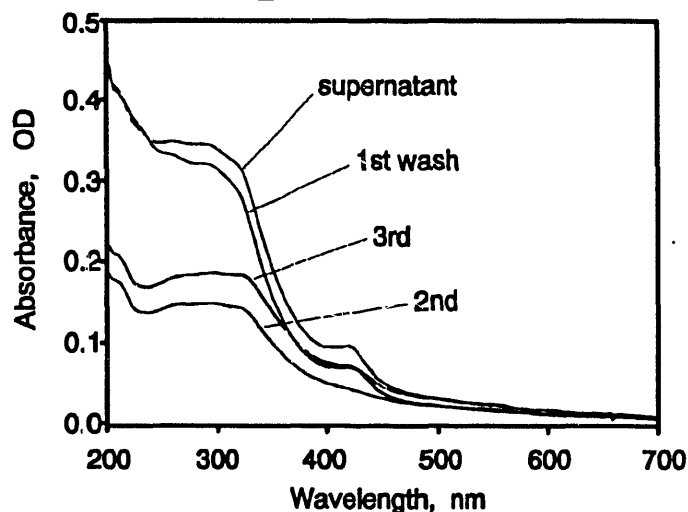


Figure 3. Successive washings of TiO_2 photosensitized by adsorption of SnUroP at pH 6.

Porphyrin-mediated colloidal dispersion of TiO_2 . In the absence of porphyrin, dispersion of fine TiO_2 particles occurs at high (>9) and low (<3) pH, but not in the pH range from 4 to 8. This is illustrated in Figure 4, 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 dispersed TiO_2 (see Figures 3 and 4). High positive (low pH) or negative (high pH) charge on the surface apparently breaks up aggregates of small TiO_2 particles resulting in the observed colloidal dispersion in the pH regions far from 6, the point of zero charge for TiO_2 ¹².

A similar process is observed in the presence of porphyrin. An increase of UV absorbance resulting from dispersion of fine TiO_2 particles is demonstrated by water washing of the porphyrin-treated TiO_2 samples shown in Figure 3. UV-visible absorption spectra of washings from samples of compositions, SnUroP/ TiO_2 /SA (added in the order indicated), and SA/ TiO_2 /SnUroP, before illumination show a significant broad absorption band from 200 nm to 340 nm which is attributed to the conduction

band absorption of the porphyrin-stabilized colloid of fine TiO_2 particles. This characteristically broad UV absorption band is also observed in the washings from the $\text{TiO}_2/\text{SnUroP}$ preparations shown in Figure 3. In contrast, the supernatant from TiO_2/SA did not exhibit this broad absorption band at pH 6.

The presence of SnUroP shifts the pH range in which colloidal dispersion occurs as illustrated in Figure 4. Dispersion occurs above pH 5, but not below. As the pK is lowered, the first of the eight acid substituents of uroporphyrin are protonated at about pH 6.6.¹³ This is also the pH range in which SnUroP starts to be adsorbed onto the surface (see Figure 4). (Although the aggregation of uroporphyrins typically is observed below pH 7 for four- and five-coordinate metal complexes, aggregation does not occur for six-coordinate metals like Sn.¹³) This suggests that either Sn uroporphyrin interacts dynamically with the surface in the pH range from 5 to 8 and the interaction results in the dispersion of TiO_2 or adsorption of SnUroP onto the surface in this range acts to maintain a high negative charge on the porphyrin modified surface. In the latter case for example, a SnUroP- x molecule (with $0 \leq x \leq 8$ acid groups deprotonated) might bind to a $-\text{OH}_2^+$ group on the surface changing the charge at that location from +1 to $1-x$, i.e., the charge of the $-\text{OH}_2-\text{SnUroP}^{-x+1}$ surface group. Thus, for more than one deprotonated group on the porphyrin, binding results in replacing the positively charged group with a negatively charged one.

Below pH 5, negatively charged carboxylate groups of the porphyrin molecule will be attracted to regions of positive charge on the TiO_2 surface. However, binding of porphyrin will now neutralize the charged regions, preventing the electrostatic repulsion that might break up aggregates of small TiO_2 particles. This is because the porphyrin substituents are nearly all protonated (and $1-x$ is close to 0). The large aromatic ring of the porphyrin also acts to modify the surface properties of the TiO_2 particles in a way that may promote aggregation of these particles. For example, when fully coated with neutral porphyrins, the surface is hydrophobic.

SnTCPP does not appear to influence as strongly as SnUroP the colloidal dispersion process, although enhanced dispersion may occur in the region between pH 5 and pH 9, the region where bare TiO_2 is not dispersed. Finally, the presence of salicylic acid does not influence the dispersion of fine TiO_2 particles, nor does its presence effect the pH dependence of the porphyrin-induced dispersion process. Its presence however may influence the degree of dispersion.

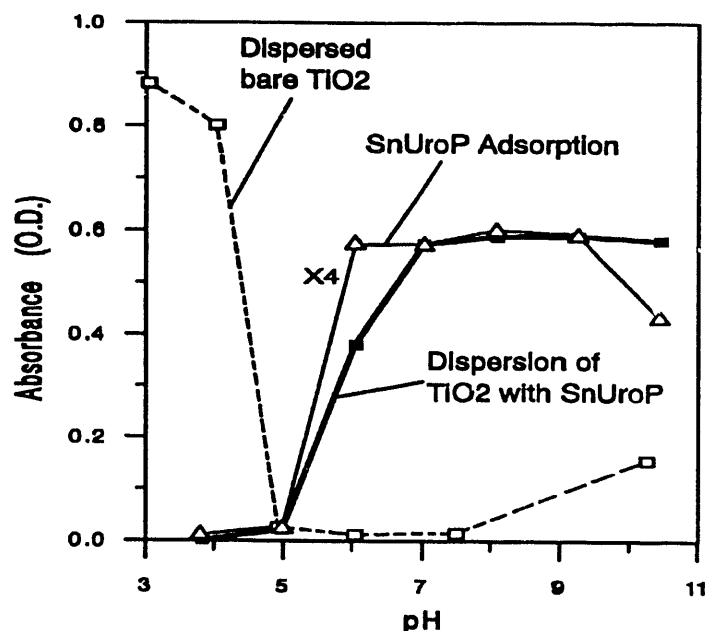


Figure 4. pH dependence of the dispersion of small TiO_2 particles for bare TiO_2 and for TiO_2 photosensitized with SnUroP (measured by the conduction band absorbance at 296 nm), and the adsorption of SnUroP onto TiO_2 (measured by the Soret band absorbance at 402 nm of the SnUroP remaining in solution).

Porphyrin modification by adsorption onto TiO_2 . As a first step in developing a

stable photosensitized TiO_2 catalyst, we compared the effects that the adsorption of the two Sn porphyrins onto the TiO_2 surface has on the porphyrin's structure. Adsorption of SnUroP was, by itself, enough to convert the porphyrin to a reduced porphyrin species, probably Sn urochlorin. The conversion can be observed by lowering the pH of a mixture of TiO_2 and an aqueous solution of SnUroP until the porphyrin is adsorbed, then raising the pH until the modified porphyrin is removed from the surface. The UV-visible spectra, obtained before and after the adsorption of porphyrin, clearly show the formation of the Sn urochlorin. In contrast with SnUroP, adsorbing SnTCPP onto the TiO_2 surface in the same way, i.e., by lowering the pH (to 4.5), does not result in conversion of the porphyrin to a reduced product.

in the absence of salicylic acid, we followed the porphyrin-mediated TiO_2 dispersion process at pH 6.0 as a function of irradiation time. The absorption due to the conduction band of colloidal dispersed TiO_2 rapidly disappears over the first 30 minutes of irradiation. This decrease in the amount of dispersed TiO_2 is most likely a result of the rapid destruction of the porphyrin, since TiO_2 dispersion does not occur at pH 6 unless porphyrin is present. Destruction of the porphyrin is confirmed visually by the bleaching of the photosensitized TiO_2 .

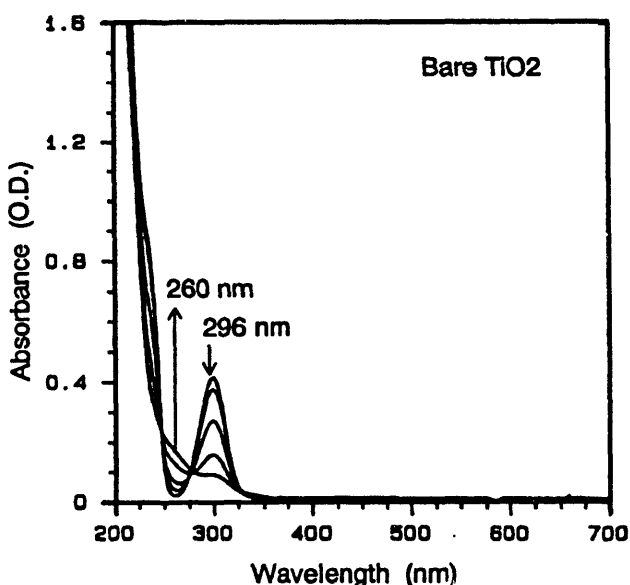


Figure 5. Change in the UV-visible absorption spectrum upon irradiation of an aqueous mixture of colloidal TiO_2 and salicylic acid at pH 5 (SA/ TiO_2). Spectra are taken at 0, 5, 20, 40, and 60 minutes.

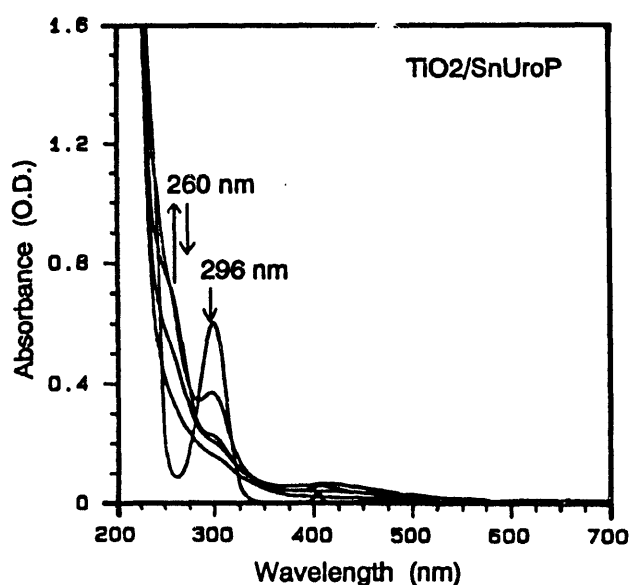


Figure 6. Change in the UV-visible absorptior spectrum upon irradiation of an aqueous mixture of tin-uroporphyrin-modified colloidal TiO_2 and salicylic acid at pH 5 (SA/ TiO_2 /SnUroP). Spectra are taken at 0, 5, 20, 40, and 60 minutes.

Enhanced photocatalytic detoxification. Enhancement of TiO_2 redox reactions that destroy toxins, by using the visible light absorbed by a photosensitizer is our primary goal. At wavelengths longer than 390 nm, weak absorption by the band edge in TiO_2 still gives formation of electron-hole pairs in the semiconductor. These holes (and electrons) normally initiate the destructive redox chemistry. For the photosensitized TiO_2 , absorption of light throughout the visible spectrum by the porphyrin results in the formation of the excited triplet state. The redox potentials of the porphyrin are altered in the excited state, and these new redox species of the excited

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

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 un-sensitized (bare TiO_2) and dye-sensitized systems are shown in Figures 5 and 6, respectively. Both the SA/ TiO_2 and SA/ TiO_2 /SnUroP mixtures were initially at pH 5 and used TiO_2 from Tioxide.

For the SA/ TiO_2 mixture, enough absorption into the edge of the conduction band occurs to generate electron-hole pairs so the destruction of the SA occurs, but at a slowed rate compared 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 peaks shows evidence of the formation of a SA degradation product. Note that clear isosbestic points are located on both sides of the 296 nm band, indicating the formation of primarily one SA degradation product that absorbs in the UV. If no intermediate were formed the absorption spectrum of salicylic acid would maintain the same shape, while decreasing in intensity as it is destroyed.

In the presence of adsorbed SnUroP, the destruction of SA by TiO_2 results in a more complicated spectral profile as shown in Figure 6. A much larger rise in the UV absorbance below 350 nm is observed and is best understood to result from the formation of a much greater concentration of the intermediate SA product. We speculate that the intermediate is similar, if not the same, as the intermediate formed at a much lower level in the absence of the porphyrin. As evidence, notice the rapid filling-in of the valley at 260 nm and the increase in the absorbance just to the red of the 296-nm SA band. The dispersion phenomenon already described may also play a role in increasing the UV absorbance, but should not be significant in the data obtained at pH 5 and shown in Figures 5 and 6.

Using the spectra illustrated in Figures 5 and 6, 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 as a function of irradiation time in Figure 7 for photosensitized TiO_2 (TiO_2 /SnUroP) and bare TiO_2 . One problem with this measure of destruction rate is that the absorbance of the SA peak at zero time for bare TiO_2 is only 69% of the SA absorbance of the photosensitized TiO_2 solution. This is in spite of the fact that the concentration of SA added is the same for both cases. Most likely, a larger fraction of the SA has adsorbed onto the bare TiO_2 surface. Almost half of the SA is bound in the case of bare TiO_2 . Upon illumination SA is destroyed on the surface, allowing more SA to adsorb from solution and, thus, contributing to the decrease in absorbance at 296 nm. The decrease in absorbance at 296 is indicative of an exponential rate of destruction of SA.

An enhanced rate of salicylic acid destruction is observed in the presence of adsorbed SnUroP on the TiO_2 surface when compared with 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.

The absorbance at 260 nm (A_{260}) is predominantly a result of formation of the

initial SA degradation product (Figure 7). In the absence of SnUroP, the absorbance shows a steady, slow increase over the first 60 minutes. In contrast, when SnUroP is present, A260 increases rapidly to a maximum in the first 30 minutes and then decreases. Thus, A260 indicates a strong initial increase in the rate of formation of the initial SA product and then its further destruction at a rate consistent with bare TiO₂.

Removal of the fine TiO₂ particles through several washings decreased the catalytic efficiency for the cases of SA/TiO₂/SnUroP, SnUroP/TiO₂/SA and TiO₂/SA at pH 6.0 (data not shown). The decrease in the efficiency of photodestruction of salicylic acid is expected, since washing removes TiO₂ photocatalyst from the system. More importantly, the improved efficiency of the composition SA/TiO₂/SnUroP (SA added before porphyrin) over SnUroP/TiO₂/SA (SA added after porphyrin) confirms that competitive adsorption between porphyrin and salicylic acid occurs as noted above and suggests that salicylic acid must be adsorbed onto the TiO₂ surface for subsequent destruction. The optimal surface coverage of the porphyrin as well as its stability on the TiO₂ surface has yet to be fully determined.

Effect of molecular oxygen.

When the experiments of Figure 7 are repeated in the absence of O₂ under a nitrogen atmosphere, almost no change in the salicylic acid spectrum is observed. This suggests that O₂ is required for both destruction of salicylic acid and formation of the SA intermediate species. SnUroP is known to photosensitize the formation of singlet O₂ with high quantum yield (~0.6),^{14,15} and singlet oxygen could be involved in formation of the SA intermediate. However, for the bare TiO₂ surface also, oxygen is required for the destruction of salicylic acid, and this requirement is maintained in the presence of the photosensitizer.

Mechanisms of photosensitization of TiO₂. A number of possible 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 TiO₂ is present. Then the enhancement would be explained if the SA product is more labile than SA.

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.

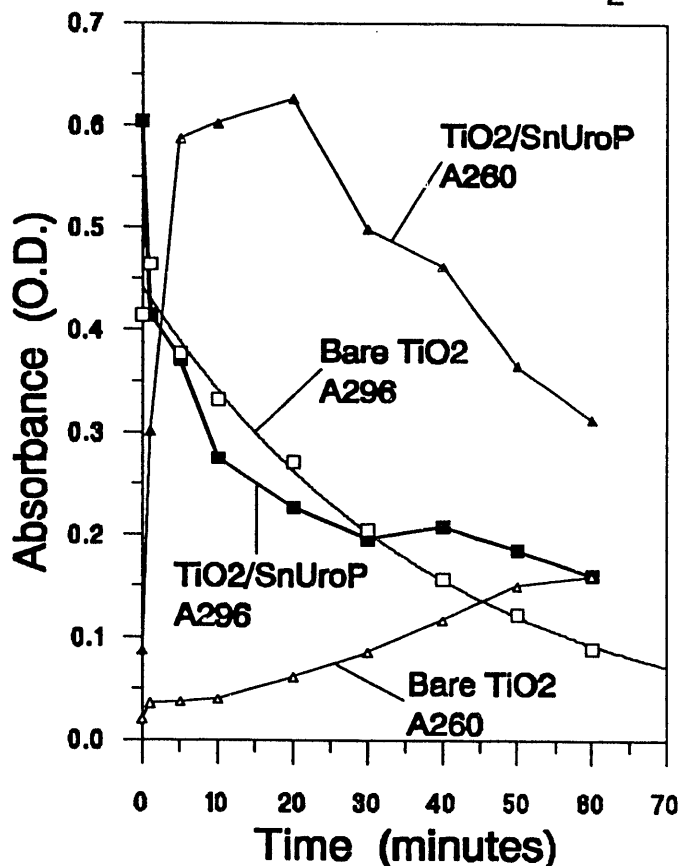


Figure 7. Enhancement of salicylic acid detoxification using Sn uroporphyrin as a photosensitizer. Salicylic acid absorbance at 296 and 260 nm (1-cm cell) is plotted against irradiation time. The curve through the data points for bare TiO₂ at 296 nm is an exponential fit.

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 .¹⁶ 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.

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 mechanism of enhancement remains to be determined.

SnUroP 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.

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