

pH-Responsive, TiO₂-Attached Porphyrin for Singlet Oxygen Production in an Aqueous Solution

Wenbing Li, Naveen Gandra, Erick D. Ellis, Shavelle Courtney, Shufang Li,[†] Ebonie Butler,[‡] and Ruomei Gao*

Department of Chemistry, Jackson State University, Jackson, Mississippi 39217

ABSTRACT A pH-responsive, TiO₂-attached sensitizer was prepared based on the adsorption of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (TCPP) onto TiO₂ nanoparticles. This colloiddally dispersed TiO₂-attached TCPP behaves as a single-phase colloidal sensitizer at pH 1.0–3.3 with quantum yields of singlet oxygen production (Φ_{Δ}) between 0.20 and 0.25, as a heterogeneous particle sensitizer at pH 3.5–6.0 with Φ_{Δ} between 0.25 and 0.50, and as homogeneous free TCPP molecules in alkaline solutions with $\Phi_{\Delta} = 0.53$. The changes in Φ_{Δ} are fully consistent with pH-dependent adsorption of TCPP onto the TiO₂ surface. Recovery yields of 99.8% for TCPP and 98.8% for TiO₂ were obtained from 1.4 mM TiO₂-attached TCPP. We attribute its photosensitization ability to retaining TCPP solubility on the TiO₂ surface and, hence, activity. This novel system shows a potential to bridge the gap between easily recoverable and highly efficient sensitizers.

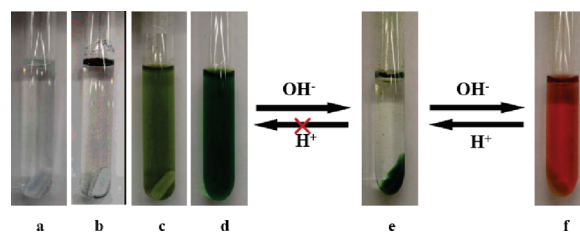
KEYWORDS: singlet oxygen • TiO₂-attached porphyrin • pH-responsive and recoverable sensitizer

1. INTRODUCTION

The use of heterogeneous sensitizers for singlet oxygen (¹O₂) photooxidation in a solution facilitates product separation and analysis. The first heterogeneous sensitizer was a polymer-attached rose Bengal synthesized by Neckers, Schaap, and their co-workers (1, 2), which was followed by a series of immobilized dyes on polymers and metal oxides (3–9). The adsorption of dye molecules onto metal oxides has been well characterized, e.g., in the field of dye-sensitized nanocrystalline TiO₂ solar cells (10–13). It is known that a homogeneous sensitizer is more efficient than its heterogeneous counterpart (2) and far less affected by limitations due to the short lifetime of ¹O₂ and the slow transport of reactants and products (14). A similar awareness existed for the use of catalysts in chemical reactions, in which strategies were developed to facilitate the recovery and recycling of homogeneous catalysts (15–22). Understanding the dependence of ¹O₂ production on dye adsorption onto support materials may bridge the gap between easily recoverable and highly efficient sensitizers and benefit areas of ¹O₂-based organic synthesis and water purification. However, such information has been limited.

In the present work, 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (TCPP) adsorption onto the TiO₂ surface was examined for its capability of ¹O₂ photosensitization. The selection of TiO₂-attached TCPP was based on its pH-

Scheme 1. Formation and Recovery of TiO₂-Attached TCPP^a



^a Sensitizer preparation at pH 2.3: (a) TiO₂ colloids before the addition of TCPP; (b) TCPP added but not yet mixed; (c) mixed for 6 h under stirring; (d) mixed for 7 days under stirring, with excess TCPP and TiO₂ removed by centrifugation. (e) TCPP and TiO₂ recovered at pH 3.5–5. (f) TCPP dissolved in the base.

responsive stability and photoactivity, as indicated in the following. (1) The substantial interaction between TiO₂ and deprotonated carboxyl groups in TCPP has been evidenced by femtosecond electron injection (23), variation in the TCPP fluorescence intensity with pH in a colloidal TiO₂ solution (24), X-ray photoelectron spectroscopy, resonance Raman spectroscopy, and the red shift in the TCPP Q band (25). Because of the strong anchoring of TCPP onto the TiO₂ surface, the electrostatic attraction between the –COO[–] groups in TCPP and the positively charged TiO₂ nanoparticles prevails at pH < 5. In an alkaline solution, where the surface charge of TiO₂ is negative, the adsorption of anionic TCPP onto the TiO₂ surface is inhibited. (2) The solubility of TCPP in an acidic solution is very low but can be greatly enhanced by adsorption onto the colloidal TiO₂ surface. Because of the pH-responsive stability and irreversible formation of TiO₂-attached TCPP, the recovery of both TCPP and TiO₂ can be simply achieved by centrifugation at certain pHs. (3) Similar to other porphyrin sensitizers, TCPP possesses the ability to produce ¹O₂ in organic solvents (toluene, methanol, and

* E-mail: ruomei.gao@jsums.edu.

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[†] A visiting scientist from College of Science at Hebei University of Science and Technology, Shijiazhuang, People's Republic of China.

[‡] A participant of the NSF-PREM summer program from Jim Hill High School, Jackson, MS.

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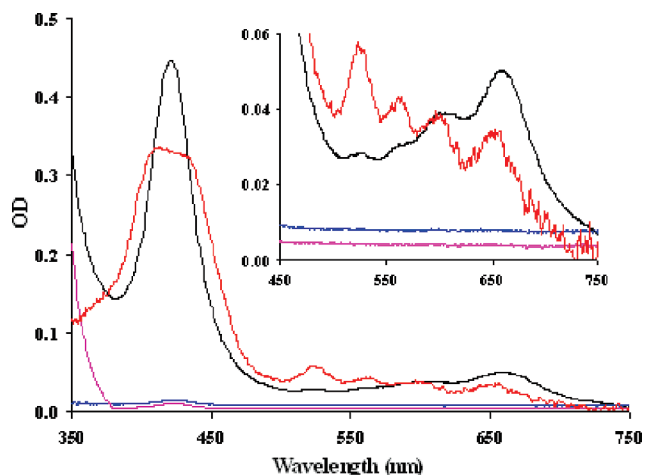


FIGURE 1. Absorption spectra of TiO_2 , TCPP, and TiO_2 -attached TCPP in pH 2.3 aqueous solutions. Black line: 5.1×10^{-5} M TCPP on 1.35×10^{-3} M TiO_2 in pH 2.3 HCl. Red line: 3.7×10^{-6} M TCPP in pH 2.3 HCl/NaOH. Purple line: 1.35×10^{-3} M TiO_2 . Blue line: TCPP supernatant from a pH 2.3 HCl-saturated TCPP solution.

Table 1. Absorption Maxima of TCPP in the Presence and Absence of TiO_2 Nanoparticles

solution	Soret bands,		Q bands, nm			
	nm					
TCPP in pH 2.3 HCl/NaOH	405–436	524	560	597	650	
TCPP in pH 10 NaOH	414	517	554	580	635	
TiO_2 -attached TCPP in pH 2.3 HCl	420	525	560	597	658	
TiO_2 -attached TCPP in pH 10 NaOH	414	517	554	580	635	

acetone) (26), in neutral water (from TCPP/cyclodextrin supramolecular complexes) (27), and in a pH 13 aqueous solution (28). Therefore, in the present work, we characterize in detail the preparation and recovery of TiO_2 -attached TCPP sensitizers and examine their photosensitization ability in a wide pH range.

2. RESULTS AND DISCUSSION

2.1. Formation and Spectroscopic Properties of a TiO_2 -Attached TCPP Sensitizer. The stability of colloidal TiO_2 nanoparticles is pH-dependent and can be measured by ζ potential. A higher ζ potential favors the formation of a stable suspension resulting from electrostatic repulsion among nanoparticles. It is well recognized that the surface of TiO_2 in an aqueous environment takes electric charges that are dependent on the pH. The positive charge occurred at acidic conditions ($\text{pH} < 5$) because of the presence of $\equiv\text{TiOH}_2^+$ groups, where the ζ potentials were sufficiently large to form stable colloids, the near-neutral charge at zero ζ potential around pH 5–7 (29, 30), and the negative charge at basic conditions ($\text{pH} > 7$) owing to $\equiv\text{TiO}^-$ groups (31), where TiO_2 precipitation from the solution was observed. Carboxylic acid functionality was the most commonly used anchoring group for dye-sensitized solar cells. These carboxylic acid groups, while ensuring efficient adsorption of dyes onto the TiO_2 surface, also promoted electronic coupling between the donor levels of the excited

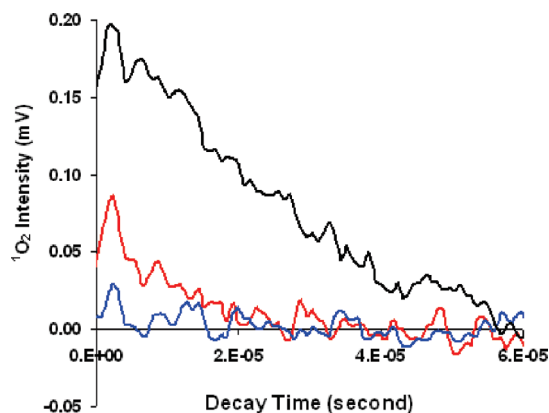


FIGURE 2. Time-resolved $^1\text{O}_2$ emission signals at 1270 nm recorded upon 532 nm irradiation of 1.5×10^{-3} M TiO_2 -attached TCPP in air-saturated 80% D_2O aqueous solutions. Black line, at pH 7; red line, at pH 3 and blue line, at pH 3 in the presence of 80 mM NaN_3 .

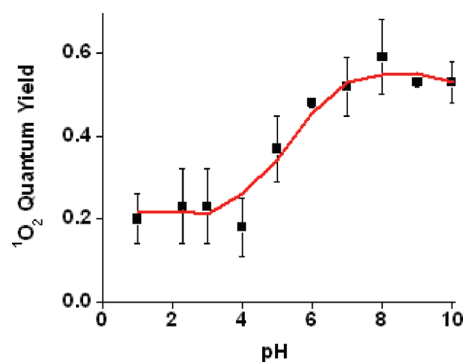


FIGURE 3. Variation in Φ_{Δ} from TiO_2 -attached TCPP with pH using TSP as a reference.

chromophore and the acceptor levels of the TiO_2 semiconductor. Some of the possible modes of chelation/derivatization ranged from chemical bonding (chelating or bridging mode) to hydrogen bonding (12). Our results showed that TiO_2 -attached TCPP colloids were extremely stable in a pH range of 1.0–3.3 (part d in Scheme 1) but aggregate at $\text{pH} > 3.5$ (part e in Scheme 1). The desorption of TCPP from the TiO_2 surface was largely enhanced in basic solutions because of the fair solubility of TCPP and electrostatic repulsion between negatively charged TiO_2 and TCPP anions (part f in Scheme 1).

The quantitative adsorption of TCPP onto the TiO_2 surface was examined by two experiments. First, an experiment was carried out in order to determine whether a decrease in the pH in the colloidal solution coincides with the adsorption of TCPP onto the TiO_2 surface. A concurrent decrease in the pH of the aqueous solution was found, which related to the deprotonation of carboxylic acid groups in TCPP upon its binding onto the TiO_2 surface. The adsorption of TCPP over 7 days corresponded to a pH reduction from 2.06 to 1.99. Because of the similar sizes of the TiO_2 nanoparticles (1 nm) and TCPP molecules (1.5 nm), it was reasonable to assume that a TCPP molecule could bind vertically on the surface of one TiO_2 nanoparticle through one of the four carboxylic acid anchoring groups. The molar ratio of $[\text{H}^+]_{\text{dissociated}}/\text{TiO}_2$ particles was found to increase from initially 0 to 1.1, which revealed an average of ca. 1 TCPP molecule per

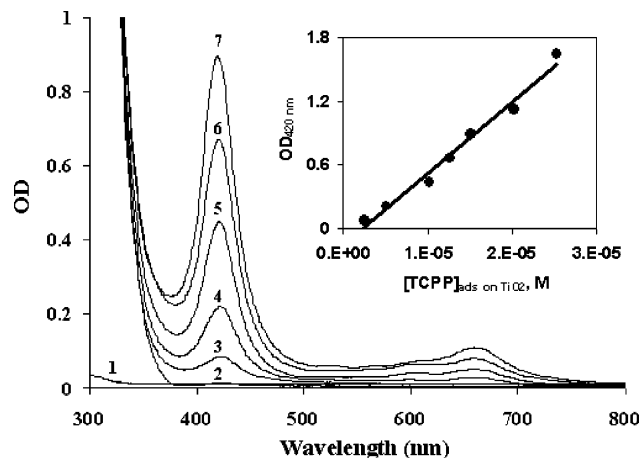


FIGURE 4. Absorption spectra and calibration curve of different amounts of TCPP adsorbed onto the TiO_2 surface in pH 2.3 aqueous solutions: 1, supernatant from saturated TCPP; 2, 2.7×10^{-4} M TiO_2 ; 3–7, 2.5×10^{-6} , 5.1×10^{-6} , 1.0×10^{-5} , 1.3×10^{-5} , and 1.5×10^{-5} M TCPP mixed with 2.7×10^{-4} M TiO_2 , respectively. Inset: calibration curve of absorbance at 420 nm vs 2.5×10^{-6} – 2.5×10^{-5} M TCPP chemisorbed on 2.7×10^{-4} M colloidal TiO_2 nanoparticles at pH 2.3.

colloidal TiO_2 nanoparticle. Second, the extinction coefficient of TCPP molecules chemisorbed onto the colloidal TiO_2 surface in a pH 2.3 aqueous solution, $\epsilon = 6.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 420 nm, was determined from the slope of a calibration curve relating the TCPP concentration to absorption (Figure 4). The amount of TCPP chemisorbed onto the TiO_2 surface was measured at 420 nm according to Lambert–Beer’s law. Typically, an average of 0.7 TCPP molecules loaded per TiO_2 particle was obtained. The loading amounts of TCPP onto the TiO_2 surface from both experiments were comparable with each other. A little bit higher value (compare 1.1 to 0.7) obtained based on pH measurements for the ratio of TCPP molecules over TiO_2 particles might result from the partial presence of two carboxylic acid anchor groups on one TiO_2 particle and/or the inconsequential decomposition of TCPP molecules during the preparation.

As shown in Figure 1, the absorption spectrum of TCPP in a pH 2.3 HCl/NaOH solution was characterized by a quite broad Soret band between 405 and 436 nm and Q bands at 524, 560, 597, and 650 nm. The protonation of the nitrogen atoms of the central macrocycle of porphyrins has been well studied. The longer-wavelength Q band becomes the most intense upon protonation, with the band diminishing in intensity in the order of decreasing wavelength (32–34). The longest-wavelength band is typical for dictations and metal complexes of porphyrin Q bands, which is reflected in the spectra of colloidal TiO_2 -attached TCPP (black line in Figure 1). TCPP was sparingly soluble in an acidic solution (blue line in Figure 1). Its solubility, however, could be improved at a low limit of ca. 6×10^{-6} M in the presence of a sodium salt (red line in Figure 1). The lowest-intensity Q band at the longest wavelength of 650 nm for TCPP in a pH 2.3 HCl/NaOH solution indicates its deprotonated spectral feature, which is probably due to the competition of sodium cations with protons for the central nitrogen atoms. In neutral and alkaline solutions, the presence of TiO_2 had hardly any effect on the Q band (Table 1), while in an acidic solution, a small

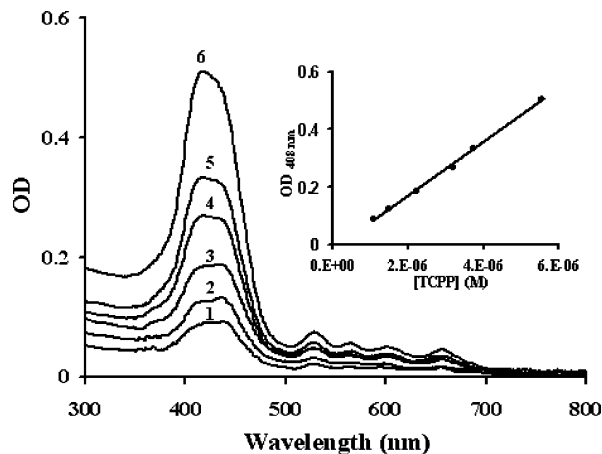


FIGURE 5. Absorption spectra and calibration curve of TCPP in pH 2.3 HCl/NaOH solutions. All spectra were measured against a pH 2.3 aqueous HCl solution: 1–6, 1.1×10^{-6} , 1.5×10^{-6} , 2.2×10^{-6} , 3.2×10^{-6} , 3.7×10^{-6} , and 5.6×10^{-6} M TCPP, respectively. Inset: calibration curve of absorbance at 408 nm vs 1.1×10^{-6} – 5.6×10^{-6} M TCPP at pH 2.3.

but reproducible red shift of the Q band at 650 nm ($650 + 8 = 658$ nm) was observed. One possible mechanism for this shift was a charge-transfer band. Coupling between the wave functions of the excited electronic state of TCPP and the charge-separated state could give mixed states (35, 36). Such a strong interaction was accomplished through chemical bonding between the TCPP central macrocycle and TiO_2 . The adsorption was also evident by the pronounced effect of pH on Φ_{Δ} (see the discussion below). A sharp change in Φ_{Δ} was observed when the pH was close to the point of zero charge (pH ~ 5.0 for TiO_2) (37), where the transition from free to surface-bound TCPP occurred. These spectral features clearly indicated the adsorption of TCPP onto the TiO_2 surface at acidic pHs and were consistent with literature reports using various techniques including femtosecond electron injection (23), fluorescence (24), X-ray photoelectron spectroscopy, resonance Raman spectroscopy, and UV/vis (25). The change in the driving force for the electron transfer might also result in an inefficient interaction between TiO_2 and TCPP molecules at higher pH. It was reasonable to suppose that the oxidation potential of porphyrin-ring-based dyes adsorbed onto the TiO_2 surface was weakly pH-dependent or pH-independent, especially in the neutral and alkaline solutions, while in TiO_2 with increasing pH, the valence and conduction band edges moved to more cathodic potentials. This would reduce considerably the driving force for charge separation (38). Therefore, we concluded that TCPP was strongly adsorbed onto the TiO_2 surface through chemical bonding at acidic pH but was released in the neutral and alkaline pH regions. The spectroscopic data are summarized in Table 1.

2.2. TCPP and TiO_2 Recovery. TiO_2 -attached TCPP remains as a homogeneous colloid at pH 1.0–3.3, a heterogeneous aggregate at pH 3.5–6.0, and free soluble TCPP molecules at pH > 7 . The formation and conversions among these forms are shown in Scheme 1. Because of pH-responsive stability and the irreversible formation of TiO_2 -attached TCPP, the recovery of both TCPP and TiO_2 was

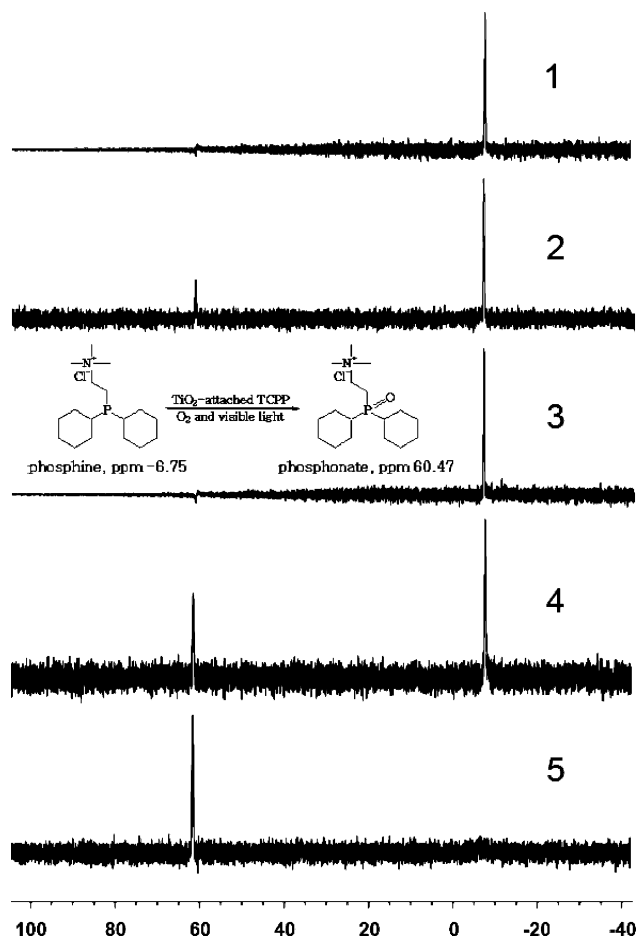
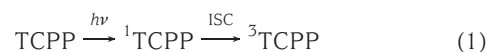


FIGURE 6. ^{31}P NMR spectra of $0.6 \mu\text{mol}$ of phosphine before and after visible light irradiation in the absence and presence of 1.00×10^{-5} M TiO_2 -attached TCPP in an O_2 -saturated 90% D_2O solution at pH 2.3: (1) phosphine before irradiation; (2) part 1 after 20 min of irradiation; (3) phosphine and TiO_2 -attached porphyrin before irradiation; (4) part 3 after 10 min of irradiation; (5) part 3 after 20 min of irradiation.

simply achieved by centrifugation at certain pHs. To test the recovery yields, a homogeneous solution of TiO_2 -attached TCPP at pH between 1.0 and 3.3 was first alkalinized with NaOH to destroy colloids, followed by centrifugation. The supernatant was analyzed at pH 2.3 to quantify the remaining TCPP and TiO_2 concentrations by monitoring TiO_2 at 215 nm using $\epsilon = 6050 \text{ M}^{-1} \text{ cm}^{-1}$ and TCPP at 408 nm using $\epsilon = 9.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (see the experimental section). The best recovery yields of 99.8% for TCPP and 98.8% for TiO_2 were obtained from 1.4 mM TiO_2 -attached TCPP by centrifugation at pH between 4 and 5.

2.3. $^1\text{O}_2$ Production and Φ_{Δ} Measurement. $^1\text{O}_2$ luminescence was detected at 1270 nm upon irradiation of TiO_2 -attached TCPP at 532 nm. The data shown in Figure 2 was assigned to $^1\text{O}_2$ phosphorescence because both the kinetics and intensity of the signals were sensitive to the concentrations of oxygen and azide ions that quench $^1\text{O}_2$ at a rate constant of $5.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in H_2O (39). Figure 2 also indicated that azide ions quench not only the lifetime of $^1\text{O}_2$ but also the initial intensity of $^1\text{O}_2$ luminescence, which can be explained by its reaction with both $^1\text{O}_2$ and the excited states of a sensitizer (40). The kinetic decay was

exponential with the rate constants (k_d) of $^1\text{O}_2$ in 80% D_2O between 1.2×10^5 and $4.4 \times 10^4 \text{ s}^{-1}$ for a pH range of 1–10. For all calculations in this work, kinetic traces have been corrected for interference from other rapid events synchronized with laser pulses (i.e., scattered light and fluorescence), using the same, except N_2 -saturated, sample as the control. Recently, we reported $^1\text{O}_2$ production upon two-photon excitation of TiO_2 in CHCl_3 at 532 nm (41). Compared to TCPP ($\Phi_{\Delta} = 0.53$ for free TCPP molecules, measured in the work), $^1\text{O}_2$ production from TiO_2 was much less efficient and could be disregarded. The generation of $^1\text{O}_2$ is based on a bimolecular sensitization reaction, represented by predominantly the triplet quenching process of a sensitizer in the presence of $^3\text{O}_2$ (eqs 1 and 2).



$^1\text{O}_2$ production upon visible irradiation of TiO_2 -attached TCPP was also evidenced by steady-state experiments using [2-dicyclohexylphosphino]ethyl]trimethylammonium chloride as a chemical trap of $^1\text{O}_2$. The loss of phosphine was monitored by ^{31}P NMR. Our results indicated that 100% conversion yields of phosphonate were obtained upon 20 min of visible irradiation of $0.6 \mu\text{mol}$ of phosphine in the presence of 1.0×10^{-5} M TiO_2 -attached TCPP at pH 2.3, wherein a homogeneous TiO_2 -attached TCPP colloid was formed. We attribute its photosensitization ability to retaining TCPP solubility on the TiO_2 surface and, hence, activity.

Φ_{Δ} is an important measure of the efficacy of $^1\text{O}_2$ photosensitization. The determination of Φ_{Δ} from a colloidal solution was not very precise because of light scattering by suspended nanoparticles. However, Φ_{Δ} could be approximated according to eq 4 by comparing the initial $^1\text{O}_2$ intensities with those from a well-developed reference sensitizer *meso*-tetrakis(sulfonatophenyl)porphyrin (TSP) using $\Phi_{\Delta} = 0.63$ in D_2O (42). TiO_2 -attached TCPP remained as a homogeneous colloidal sensitizer at pH between 1 and 3.3 but aggregated in a pH range of 3.5–6. In neutral and basic solutions, $^1\text{O}_2$ mainly resulted from free TCPP molecules. Φ_{Δ} exhibited in the sigmoidal curve was pH-dependent and fully consistent with pH-dependent TCPP adsorption onto the TiO_2 surface (Figure 3). An observed sharp change in Φ_{Δ} took place when the pH was close to the point of zero charge (pH ~ 5.0 for TiO_2) (37), where the transition from free to surface-bound TCPP occurred. The higher Φ_{Δ} value obtained in neutral and alkaline solutions (0.54 from Figure 3) was perfectly in agreement with both our value 0.53 for free TCPP measured in a pH 10 NaOH solution and the literature value 0.47 determined at pH 13 (28). Similar observations were reported for weak fluorescence quenching at higher pH performed by Hartland for anthracene dyes bound to TiO_2

(43) and for weak electron transfer in alkaline solutions studied by Gratzel for zinc porphyrin in a colloidal TiO₂ solution (44). We therefore concluded that efficient energy transfer from ³TCPP to ³O₂ in neutral and alkaline conditions was due to the lack of adsorption of anionic TCPP onto a negatively charged TiO₂ surface. The electron transfer between TiO₂ and TCPP could compete favorably with the energy-transfer process in acidic conditions, subsequently resulting in lower Φ_A.

2.4. Effects of TiO₂ Surface Coverage on the Quenching Rates of ¹O₂. To quantify the apparent quenching of ¹O₂, the total rate constants of ¹O₂ removal (*k_T*) by free TCPP and TiO₂-attached TCPP were determined by Stern–Volmer analysis using TSPP as a sensitizer. *k_T* = (1.1 ± 0.1) × 10⁸ M⁻¹ s⁻¹, measured from TiO₂-attached TCPP in a pH 2.3 HCl solution, was comparable to those from other porphyrin sensitizers, e.g., 6 × 10⁷ M⁻¹ s⁻¹ for TPP in C₆D₆ (45) and <10⁸ M⁻¹ s⁻¹ for free and metallo-TSPP in D₂O (46). A higher value of (1.1 ± 0.1) × 10⁸ M⁻¹ s⁻¹ for TiO₂-attached TCPP than that of (5.0 ± 0.1) × 10⁷ M⁻¹ s⁻¹ for free TCPP measured in a pH 10 NaOH solution might result from fast quenching of ¹O₂ by TiO₂ nanoparticles (41).

3. CONCLUSION

TiO₂-attached TCPP retained its photosensitization ability in a wide pH range, e.g., as a homogeneous colloid at pH between 1.0 and 3.3, a heterogeneous aggregate in a pH range of 3.5–6.0, and free soluble TCPP molecules at pH >7. Both TCPP and TiO₂ could be easily separated from solutions by centrifugation at pH between 3.5 and 5 with satisfied recovery yields. This pH-responsive, TiO₂-attached TCPP has advantages of high dispersion and subsequent efficient ¹O₂ production. The novel system shows a potential to bridge the gap between easily recoverable and highly efficient sensitizers. Also, it provides a general methodology for the separation of dyes based on their interaction with inorganic metal oxides. The recoverable sensitizers can be of great significance to aqueous phase organic synthesis, water detoxification, and disinfection. Because of the photocatalytic activity of TiO₂ under UV illumination, the application of TiO₂-attached TCPP should be restricted to visible light. A challenge for future development is to tailor recoverable sensitizers with the aim of using a wide range of light energy for photosensitization.

4. MATERIALS AND METHODS

Materials and Instrumentation. Reagents and solvents were obtained commercially and used without further purification. *meso*-Tetrakis(4-carboxylphenyl)porphine (TCPP) and *meso*-tetrakis(4-sulfonatophenyl)porphine dihydrochloride (TSPP) were purchased from Frontier Scientific, Inc., and [2-(dicyclohexylphosphino)ethyl]trimethylammonium chloride (>98%) from Strem Chemicals, Inc., a 1.005–0.995 M standard NaOH solution from Fisher Scientific, D₂O (99% atom) from Sigma-Aldrich, and sodium azide (99%) from Acros Organics. Deionized water was obtained from a Nanopure Water (Barnsted System). A Q-switched Nd:YAG laser with a pulse duration of 3–4 ns and a maximum energy of 30 mJ at 532 nm (Polaris II-20, New Wave Research MerchanteK Products) and a liquid-N₂-cooled germanium photodetector (Applied Detector Corp.) were used

for time-resolved ¹O₂ luminescence measurements. Steady-state photooxidation was conducted in an O₂-saturated solution using a 300 W Hg lamp (Newport Oriel Instruments, 68911 arc lamp power supply, 200–500 W Xe/HgXe) equipped with a water filter and a 500 nm cutoff filter. Other instruments employed in this research include a BioMate 3 UV/vis spectrophotometer (Thermo Scientific) or a Cary 300 UV/vis spectrophotometer (Varian, Inc.) for taking absorbance and spectra and a centrifuge (Fisher Scientific, Inc, Centrifug model 228) for heterogeneous separation. Determinations of the photooxidation products were done with a 300 MHz Bruker Spectrospin FT-NMR and/or a 400 MHz JEOL Eclipse FT-NMR. All measurements were carried out at ambient temperature.

Colloidal TiO₂ Preparation and Concentration Determination. Colloidal TiO₂ solutions were prepared by hydrolysis of TiCl₄ as previously described (47, 48). Briefly, 2.5 mL of TiCl₄ at 0 °C was introduced under a stream of N₂ and vigorous stirring into 70 mL of a water/ice solution of 0.1 M HCl. After 30 min of stirring at 0 °C, the solution was dialyzed against aqueous HCl of pH 2.3 using Spectrapor membrane tubing (Spectrum Medical Industries) with MW 6000–8000 cutoff pores. A transparent solution containing ca. 20 g L⁻¹ of TiO₂ at pH 2.3 was obtained. The molecular TiO₂ concentration was determined by spectrophotometric measurements at 215 nm using a molar extinction coefficient of 6050 M⁻¹ cm⁻¹ (47). The solution was kept in a refrigerator at 2–5 °C and used within 3 months. Colloidal TiO₂ nanoparticles thus prepared had an average diameter of 1.0 nm, with 90% of the diameters in the range 0.8–1.3 nm (48). TiO₂ concentrations were reported in terms of TiO₂ particles (*C*_{TiO₂ particles}, M) to better reflect the experimental conditions. The particle concentration was calculated according to eq 1 using a TiO₂ density (*d*_{TiO₂}, g cm⁻³) of 4 g cm⁻³ and an average diameter (*φ*_{TiO₂}, nm) of 1.0 nm.

$$C_{\text{TiO}_2 \text{ particles}}, \text{ M} = \frac{\left(\frac{C_{\text{TiO}_2}, \text{ g L}^{-1}}{d_{\text{TiO}_2}, \text{ g cm}^{-3}} \right) \left[\frac{4}{3} \pi \left(\frac{\phi_{\text{TiO}_2}, \text{ nm}}{2} \times 1 \times 10^7 \right)^3 \right]}{6.02 \times 10^{23}} \quad (3)$$

Preparation of TiO₂-Attached TCPP Colloids and Concentration Determination. TiO₂ nanoparticles modified with TCPP molecules were prepared by mixing 0.0063 g of TCPP with 20.00 mL of a pH 2.3, 1.7 g L⁻¹ solution of colloidal TiO₂ for 7 days under stirring. The mixture was kept in the dark during preparation to avoid photocatalytic decomposition of TCPP. The excessive TiO₂ particles and TCPP molecules were then separated from the aqueous phase by centrifugation. TiO₂-attached TCPP colloids thus prepared were extremely stable in the pH range of 1.0–3.3 with an extinction coefficient of ε = 6.8 × 10⁴ M⁻¹ cm⁻¹ at 420 nm measured at pH 2.3. For extinction coefficient measurement, 100% adsorption of TCPP onto the TiO₂ surface was required. We therefore used a minimum 10-fold excess of TiO₂ particles relative to the TCPP molecular concentrations. The remaining TiO₂ particles were removed from the solution by centrifugation. The absorption spectra and calibration curve are shown in Figure 4. All spectra were measured against a pH 2.3 aqueous HCl solution. The amount of TCPP chemisorbed onto the TiO₂ surface was therefore determined at 420 nm according to Lambert–Beer's law using ε_{420 nm} = 6.8 × 10⁴ M⁻¹ s⁻¹. Typically, an average load of 1 TCPP molecule per TiO₂ particle was obtained.

Determination of the Remaining TCPP Concentration in the Solution. TCPP was nearly insoluble in an acidic solution (blue line in Figure 1). Its solubility, however, could be improved at a low limit of ca. 6 × 10⁻⁶ M in the presence of a sodium

salt. A series of standard TCPP solutions at pH 2.3 were therefore prepared by first dissolving TCPP in pH 10 NaOH/H₂O, followed by acidifying the solution to pH 2.3 with HCl. The recovery of TiO₂-attached TCPP aggregates was achieved by centrifugation at pH between 4 and 5. The remaining TCPP concentrations were therefore calculated according to Lambert–Beer's law using $\epsilon = 9.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ measured at 408 nm in a pH 2.3 acidic solution, as shown in Figure 5.

Φ_{Δ} Measurement. Φ_{Δ} values were determined in aerated solutions by comparing the intensity of ¹O₂ phosphorescence at 1270 nm from TiO₂-attached TCPP with that from a reference sensitizer TSPP in D₂O using a known $\Phi_{\Delta, \text{TSPP}} = 0.63$ (42). ¹O₂ phosphorescence at 1270 nm was monitored as previously described (49). The initial ¹O₂ intensity was extrapolated to time zero and corrected by using the same, except N₂-saturated, sample as the control. The data points of the initial 3–5 ns were not used because of electronic interference signals from the detector. The absorbances of TiO₂-attached TCPP and TSPP were determined to be the same at an excitation wavelength of 532 nm. Φ_{Δ} values were calculated according to eq 4.

$$\frac{\Phi_{\Delta, \text{TiO}_2\text{-attached TCPP}}}{\Phi_{\Delta, \text{TSPP}}} = \frac{I_{\Delta, \text{TiO}_2\text{-attached TCPP}}}{I_{\Delta, \text{TSPP}}} \quad (4)$$

Here $\Phi_{\Delta, \text{TiO}_2\text{-attached TCPP}}$ and $\Phi_{\Delta, \text{TSPP}}$ are the Φ_{Δ} values from TiO₂-attached TCPP and TSPP, respectively, and $I_{\Delta, \text{TiO}_2\text{-attached TCPP}}$ and $I_{\Delta, \text{TSPP}}$ the ¹O₂ intensities from TiO₂-attached TCPP and TSPP, respectively.

Determination of the Total Quenching Rate Constants of ¹O₂ Removal by Stern–Volmer Analysis. Many sensitizers also quench ¹O₂ via chemical and/or physical reactions. In order to quantify the apparent strong quenching of ¹O₂ by TiO₂-attached TCPP, we determined the total quenching rate constant of ¹O₂ removal (k_T) for both colloidal TiO₂ particles and TiO₂-attached TCPP by Stern–Volmer analysis. The quenching rate constants were calculated in terms of TiO₂ particle concentrations. Measurements were carried out at 532 nm excitation using TSPP in pH 2.3 D₂O as the sensitizer. Considering relatively low concentrations of TiO₂-attached TCPP used in quenching experiments and high Φ_{Δ} from TSPP (42), ¹O₂ signals resulting from TCPP could be disregarded when compared with those from TSPP. Our data indicated that the kinetics of ¹O₂ luminescence decay at 1270 nm followed the Stern–Volmer equation (eq 5).

$$k = k_d + k_T[Q] \quad (5)$$

where k is the observed first-order rate constant of ¹O₂ decay after laser pulse, k_d the first-order rate constant of ¹O₂ decay in the absence of a quencher, k_T the second-order rate constant for bimolecular quenching of ¹O₂, or the total quenching rate constant of ¹O₂ removal. Changes in the ¹O₂ lifetimes were observed by the addition of TiO₂ particles or TiO₂-attached TCPP to the solutions. Stern–Volmer plots gave a good linear correlation between k and quencher concentration [Q]. k_T values then could be derived from the slopes of the straight lines.

Photooxidation of [2-Dicyclohexylphosphino)ethyl]trimethylammonium Chloride. ¹O₂ photooxidation of phosphines led to the formation of either phosphonate or a mixture of phosphonate and phosphinate (50, 51). A water-soluble phosphine, [2-(dicyclohexylphosphino)ethyl]trimethylammonium chloride, was employed as a ¹O₂ trap in steady-state photolysis experiments. Photooxidation products were determined by ³¹P NMR, as previously reported (50, 51). The reactions were carried out in the presence of $1.00 \times 10^{-5} \text{ M}$ TiO₂-attached TCPP in an O₂-saturated 90% D₂O solution at pH 2.3. ¹O₂ photooxygen-

ation led to the formation of a sole product, phosphonate (Figure 6). The percent yields were calculated by comparison of the integrated ³¹P NMR peaks of phosphine with those of phosphonate in ³¹P NMR spectra. Control experiments were carried out in order to correct phosphine oxidation by ground-state oxygen molecules (line 2 in Figure 6). Examples of ³¹P NMR spectra shown in Figure 6 indicated peaks of phosphine, $\delta -6.75$ (s, 1P), and phosphonate, $\delta 60.47$ (s, 1P).

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