Visible-Light Activation of a Dissolved Organic Matter–TiO₂ Complex Mediated via Ligand-to-Metal Charge Transfer

Hoang Tran Bui, Hyeon Yeong Park, Pedro J. J. Alvarez, Jaesang Lee, Wooyul Kim, and Eun-Ju Kim

ABSTRACT: Given the widespread use of TiO₂, its release into aquatic systems and complexation with dissolved organic matter (DOM) are highly possible, making it important to understand how such interactions affect photocatalytic activity under visible light. Here, we show that humic acid/TiO₂ complexes (HA/TiO₂) exhibit photoactivity (without significant electron–hole activation) under visible light through ligand-to-metal charge transfer (LMCT). The observed visible-light activities for pollutant removal and bacterial inactivation are primarily linked to the generation of H₂O₂ via the conduction band. By systematically considering molecular-scale interactions between TiO₂ and organic functional groups in HA, we find a key role of phenolic groups in visible-light absorption and H₂O₂ photogeneration. The photochemical formation of H₂O₂ in river waters spiked with TiO₂ is notably elevated above naturally occurring H₂O₂ generated from background organic constituents due to LMCT contribution. Our findings suggest that H₂O₂ generation by HA/TiO₂ is related to the quantity and functional group chemistry of DOM, which provides chemical insights into photocatalytic activity and potential ecotoxicity of TiO₂ in environmental and engineered systems.

KEYWORDS: titanium dioxide nanoparticles, humic acid, ligand-to-metal charge transfer (LMCT), visible light, hydrogen peroxide

INTRODUCTION

Titanium dioxide (TiO₂) comprises a high fraction of nanoparticle production due to its widespread use in consumer and industrial products. Potential environmental impacts of TiO₂ have been widely assessed under UV illumination because titania, a wide band-gap semiconductor (3.0–3.2 eV), only absorbs UV light (<5% of sunlight). However, limited attention has been given to the effects of TiO₂ upon exposure to visible light in the presence of photosensitizing dissolved organic matter (DOM) that abounds in natural waters.

Photosensitization is an effective approach to extend the photoresponse of TiO₂ to the visible-light region. Two types of photosensitization processes may be used: dye sensitization and ligand-to-metal charge transfer (LMCT) sensitization. Dye sensitization occurs via the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital photoexcitation of a dye, followed by an electron transfer from the dye-excited state to the conduction band (CB) of TiO₂ while the LMCT sensitization involves a visible-light-induced electron transfer from the HOMO of adsorbates to the TiO₂ CB (Scheme S1). Unlike dye sensitization where the dye must absorb visible light, the adsorbate in LMCT sensitization does not have to absorb visible light. Various organic and inorganic compounds with diverse functionalities have been used to form visible light-responsive LMCT complexes with TiO₂.

DOM is characterized by a large mixture of organic molecules containing carboxyl, phenolic, hydroxyl, quinone, and nitrogen- and sulfur-containing functional groups, some of which are chromophores. Given the favorable adsorption of DOM onto TiO₂ surfaces through electrostatic attraction and ligand exchange, DOM is likely to form LMCT complexes on TiO₂. The molecular structure of a ligand determines the binding mode to the TiO₂ surface, which in turn, affects the electronic coupling strength. For example, catechol formed relatively strong electronic coupling with TiO₂ compared to salicylate. We postulate that the mechanism of reactive oxygen species (ROS) generation varies depending on the electronic coupling of the ligand with TiO₂. Controlling the ROS formation (mainly, singlet oxygen (¹O₂), superoxide...
Photocatalytic Experiments and Sample Analysis. Photocatalytic experiments were conducted in a 30 mL pyrex reactor with a quartz window (40 mm diameter) containing aqueous suspensions of TiO\textsubscript{2}, HA, and target pollutants (4-CP, Cr(VI), DCA, or E. coli) at pH 3 (±0.05) under visible-light irradiation. The external light was provided by a 300 W Xe arc lamp (Oriel) equipped with a 10 cm IR water filter and a cutoff filter (λ > 320 nm and λ > 420 nm for UV and visible-light irradiations, respectively), and the typical incident light intensity was determined to be approximately 100 mW cm\textsuperscript{-2}. Simulated sunlight was provided by an AM 1.5 G solar simulator (Oriel). Prior to irradiation, the suspension was stirred in the dark for 20 min to ensure adsorption equilibrium. Sample aliquots were withdrawn from the reactor at predetermined time intervals using a 1 mL syringe and filtered through a 0.45 μm PTFE filter (Millipore). The degradation of 4-CP was monitored using a high-performance liquid chromatography (Shimadzu, LC-20AD pump) system combined with a diode array detector and a Shim-pack GIS column (4.6 mm × 250 mm). A mixture of 0.1% H\textsubscript{2}PO\textsubscript{4} solution and can at 60:40 was used as the eluent. The reduction of Cr(VI) was analyzed by the colorimetric DPC method. The absorption of the Cr–DPC complex at 540 nm was monitored using a UV–vis spectrophotometer (Sincos S-3100).\textsuperscript{23} Quantification of DCA was performed using an ion chromatograph (Thermo Dionex Aquion)-conductivity detector combined with a Dionex IonPac AS 22 (4 mm × 150 mm) column. The eluent solution was 3.5 mM Na\textsubscript{2}CO\textsubscript{3}/1 mM NaHCO\textsubscript{3}. Bacterial inactivation efficiency was determined by counting the colonies on agar plates before and after treatment.

Characterizations. TiO\textsubscript{2} samples were characterized before and after HA adsorption using scanning electron microscopy (SEM, Hitachi Regulus 8230), X-ray diffraction (XRD, Bruker D8-ADVANCE), X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI 5000 Versa Probe system), and Fourier transform infrared (FTIR) spectroscopy (Bruker Vertex 80v). The optical absorption spectra of the HA, TiO\textsubscript{2}, and TiO\textsubscript{2}/HA complex (HA/TiO\textsubscript{2}) powders were recorded using a diffuse reflectance UV–vis spectrophotometer (DR–UVS). Photocurrent generation was measured using a TiO\textsubscript{2}/FTO electrode prepared by the doctor blade method in 0.5 M NaClO\textsubscript{2} at pH 3. The TiO\textsubscript{2}/FTO, Pt, and Ag/AgCl electrodes were used as working, counter, and reference electrodes, respectively. The HA solution was spiked in the electrolyte three times to gradually increase its concentration (2.5, 5, and 10 mg/L). Photocurrents were measured at a constant potential (0.145 V) using a potentiosit (Metrohm AG). Steady-state photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (Hitachi F-7000) with an excitation wavelength of 400 nm. Time-resolved PL decay traces were obtained by a time-correlated single-photon counting system (PicoQuant Flutin 200) with a 1 MHz repetition rate. The samples were excited by a 375 nm laser source, and the emitted PL was collected by a photon multiplier tube detector (PicoQuant PMA 182) at 520 nm.

ROS Quantification. The production of *OH was monitored by fluorescence measurements using HPF and coumarin as *OH trapping agents. The fluorescence emission intensity of HPF was measured using a spectrophotometer (JASCO, FP-8500) at 515 nm following excitation at 490 nm. Fluorescence emission of 7-hydroxycoumarin, a hydroxylated product of coumarin, was measured at 460 nm following excitation at 332 nm. The quantitative analyses of O\textsubscript{2}•− and anion radical ("O\textsubscript{2}•−") and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and hydroxyl radical ("OH") in the photocatalytic system is critical because these species are implicated in a variety of processes in aquatic environments, including degradation of organic pollutants and inactivation of bacteria and viruses.\textsuperscript{21,22} However, the ligand heterogeneity of DOM often hinders the determination of the exact role of specific functional groups in surface complexion with TiO\textsubscript{2}. Thus, understanding complexion at the molecular level could provide valuable insight into DOM chemistry that controls LMCT sensitization and ROS generation.

The present study reports that humic acids (HAs) can form a LMCT band on the TiO\textsubscript{2} surface (from ca. 400 nm to ca. 650 nm), which enables the TiO\textsubscript{2}/HA complex (HA/TiO\textsubscript{2}) to harvest the visible light successfully. The remarkable performance of HA/TiO\textsubscript{2} for the removal of various pollutants and the inactivation of waterborne bacteria is ascribed to the enhanced generation of ROS, mainly H\textsubscript{2}O\textsubscript{2} under visible-light irradiation (λ > 420 nm). These results infer the involvement of the CB electron-induced reduction process only in the LMCT sensitization, thus minimizing the oxidative consumption of H\textsubscript{2}O\textsubscript{2} by photogenerated valence band holes. To probe the role of HA chemistry in the LMCT process as an alternative sensitization, we further evaluate the visible-light absorption and H\textsubscript{2}O\textsubscript{2} generation of TiO\textsubscript{2}–organic ligand complexes. The data presented here focus on the simple functional groups of HA as a starting point and highlight the importance of the quantity and composition of DOM in controlling H\textsubscript{2}O\textsubscript{2} generation in the photocatalytic system.

### MATERIALS AND METHODS

**Materials.** The following reagent-grade chemicals were used: 4-chlorophenol (4-CP, Sigma-Aldrich), N,N-diethyl-1,4-phenylene-diamine sulfate (DPS, Sigma-Aldrich), horseradish peroxidase (Sigma-Aldrich), phosphoric acid solution (Sigma-Aldrich), 2,3-bis-(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-carboxanilide (XTT, Sigma-Aldrich), sodium dichromate dihydrate (Na\textsubscript{2}CrO\textsubscript{4}, Sigma-Aldrich), tert-butyl alcohol (TBA, Sigma-Aldrich), 1,5-diphenylcarbazide (DPC, Sigma-Aldrich), sodium perchlorate (NaClO\textsubscript{2}, Sigma-Aldrich), aniline (Sigma-Aldrich), pthalic acid (Sigma-Aldrich), thio-phenol (Sigma-Aldrich), pyrocatechol (Sigma-Aldrich), sodium dichloroacetate (DCA, Sigma-Aldrich), 5,5-dimethyl-1-pyrroline N-oxide (DMPO, Sigma-Aldrich), coumarin (Sigma-Aldrich), sodium fluoride (NaF, Sigma-Aldrich), superoxide dismutase (SOD, Sigma-Aldrich), catalase (CAT, Sigma-Aldrich), dibasic sodium phosphate heptahydrate (Samchum), monobasic sodium phosphate (Kanto), 3′-(p-hydroxyphenyl)-flourescein (HPF, Thermo Fisher), and hydrogen peroxide solution (H\textsubscript{2}O\textsubscript{2}, Junsei). TiO\textsubscript{2} (Evonik Degussa P25) and Suwannee River HA [SRHA, International Humic Substances Society (IHSS)] were used in all the experiments. The HA concentration was measured as dissolved organic carbon using a total organic carbon analyzer (Shimadzu TOC-LCPH E200 ROHS). Escherichia coli (KCTC 2571) was supplied by the Korean Collection for Type Culture (KCTC). All solutions and suspensions were prepared using ultrapure deionized water (>18 MΩ-cm), produced by a Barnstead purification system (Thermo Scientific). The river water sample was collected from the Han River in Yangpyeong (Korea) and filtered through a 0.45 μm membrane (Millipore). A summary of the river water physicochemical characteristics is provided in Table S1.

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10830
H₂O₂ were performed on a UV−vis spectrophotometer, using the XTT-formazan production and DPD methods, respectively. 26,27 Electron paramagnetic resonance (EPR) spectroscopy (Bruker ELEXYS E580) was employed to detect the ROS captured by the DMPO reagent.

Statistical Analyses. All experiments were performed in triplicate (or more replicates), and Student’s t-test (two-tailed) was used to determine if the differences were significant (i.e., p < 0.05). Data were presented as mean ± standard deviation.

RESULTS AND DISCUSSION

Visible-Light Activity of HA/TiO₂. Control tests with either TiO₂ or HA alone did not significantly remove 4-CP, Cr(VI), and E. coli under visible light (Figure 1a−c)—except for a small amount of 4-CP removed by visible-light-illuminated TiO₂, which was likely facilitated by direct electron transfer from adsorbed 4-CP to the TiO₂ CB. 28 In contrast, HA/TiO₂ exhibited remarkable visible-light activities for 4-CP degradation, reduction of Cr(VI) to Cr(III), and E. coli inactivation (Figure 1a−c). After 2 h of irradiation, the removal of TOC associated with 4-CP reached 55% in the HA/TiO₂ suspension, compared to only 10% for TiO₂ alone, suggesting that some 4-CP was mineralized by HA/TiO₂ under visible light. In addition, significant photoreduction of Cr(VI) by HA/TiO₂ was achieved even in the presence of O₂, another electron acceptor. This is likely related to the fact that Cr(VI) reduction is thermodynamically more favorable than that of O₂. 29

We ruled out the possibility that UV light leaking from the cutoff filter may contribute to the observed pollutant removal, given the negligible degradation of DCA in visible light (Figure S1). Therefore, the mechanism of organic degradation and bacterial inactivation by HA/TiO₂ under visible-light irradiation must be different from that under UV light, which is known to involve OH radicals. To verify this, we examined the effect of TBA as an OH radical scavenger on the degradation of 4-CP by HA/TiO₂ under UV or visible-light irradiation (Figure S2). TBA significantly hindered 4-CP degradation under UV light but had little impact under visible light, which infers that 4-CP degradation under visible light occurred via a different pathway not involving OH radicals.

A photocatalytic reaction typically causes oxidative stress in bacterial cells owing to the generation of ROS, which leads to cellular damage and ultimately cell death. 30 To address the relationship between visible-light-induced bactericidal activity and oxidative stress, we probed the ROS level in E. coli using a fluorescent probe (H2DCFDA). The generation of intracellular ROS was significant only in cells treated with HA/TiO₂ (Figure 1d). These results demonstrate that HA/TiO₂ can exert oxidative stress under visible light, resulting in the observed cytotoxicity to E. coli.

Formation of the Visible-Light-Absorbing Surface Complex. Adsorption of HA on TiO₂ is a requirement for efficient electron transfer. The HA adsorption isotherm on TiO₂ at pH 3 is shown in Figure S3a. At pH 3, almost all of the HAs were adsorbed on TiO₂ in the range of 2.5−20 mg/L HA, as shown by the linear portion of the curve. The net surface charge of TiO₂ and HA was opposite at low pH, as indicated by zeta potential measurements (Figure S3b). This results in electrostatic attraction that enhances HA adsorption onto
TiO₂. However, HA adsorption propensity decreases at near-neutral pH as the magnitude of the opposing zeta potentials of TiO₂ and HA decrease significantly (Figure S3b). The observed decrease in 4-CP and Cr(VI) removal efficiency by visible-illuminated HA/TiO₂ at pH 6 compared to pH 3 (Figure S4) corroborates the importance of adsorption of HA onto the TiO₂ surface in the process.

SEM images (Figure S5a,b) and XRD patterns (Figure S5c) of TiO₂ and HA/TiO₂ showed that HA adsorption did not induce a morphological change or phase transformation in the bare TiO₂. HA/TiO₂ exhibited a BET surface area of 53 m²/g, which was not significantly affected by HA adsorption compared to that of bare TiO₂ (56 m²/g). The chemical interaction between HA and TiO₂ was investigated by XPS analysis. The high-resolution C 1s spectrum of HA/TiO₂ could be resolved into three peaks, corresponding to C==C (284.6 eV), C–O (285.6 eV), and O==C==O (288.4 eV) (Figure S5d). The high-resolution O 1s spectrum corroborated with the data for the C 1s spectrum and revealed the presence of the peak at 529.5 eV (Figure S5e) attributed to Ti–O−−O, indicating the importance of such bonds in the surface complex formation between HA and TiO₂. The formation of the HA−TiO₂ complex through ligand adsorptions of phenolic and carboxylic groups was further supported by the occurrence of several prominent peaks at 1060, 1380, 1450, and 1610 cm⁻¹ in the FTIR spectrum (Figure S5f), which can be assigned to C−O stretching of alcohol functional groups, C−O stretching of phenolic OH groups, aromatic C−C bands, and COO− asymmetric stretching.

The photocurrent generated as a function of HA concentration was monitored at the TiO₂/FTO electrode under visible-light illumination with HA than without HA (Figure 2a). Moreover, the gradual increase in the photocurrent intensity with the HA concentration might come from electron transfer from adsorbed HA to the TiO₂ CB. Steady-state and time-resolved PL measurements were performed to gain additional insight into the electron transfer between HA and TiO₂. Figure S6a shows a strongly quenched PL emission of HA in the presence of TiO₂. The PL intensity of HA decreased more significantly with increasing TiO₂ concentrations, indicative of the promoted electron transfer from HA to the TiO₂ CB. Since HA serves as an electron donor in our system, HA may be oxidized and degraded. However, we could not detect any sign of HA degradation during visible-light irradiation (Figure S7), which is related to the supramolecular structure of HA that has comparable electron-accepting/donating capacity. The time-resolved decay profile of HA and HA/TiO₂ in Figure S6b could be fitted with a biexponential or triexponential function (Table S2). The average PL lifetimes for HA and HA/TiO₂ were calculated to be ~1.3 and 0.6 ns, respectively. The shortened average lifetime and the emergence of an additional fast component (τ₁) in HA/TiO₂ corroborate the interfacial electron transfer between HA and TiO₂.

The DR UV−vis absorption spectra of TiO₂ and HA/TiO₂ at pH 3 and pH 6.6 revealed similar absorption patterns (Figures 2b and S8). In contrast to TiO₂ that showed no absorption signature in the visible range, HA/TiO₂ exhibited a broad absorption in the region of λ > 400 nm tailing to around 650 nm (Figures 2b and S8). The absorption pattern of HA alone exhibited an exponential decrease in absorbance with increasing wavelength and almost no absorbance above 500 nm (inset of Figure 2b). Thus, the more pronounced absorption of HA/TiO₂ in the lower-energy region can be attributed to the LMCT transition from the adsorbed HA to Ti(IV) on the TiO₂ surface. In support of this explanation, the visible-light absorption was obviously decreased when the HA/TiO₂ surface was modified with phosphate or fluoride (Figure S9a), which is in accordance with the reduction of 4-CP photodegradation rates by HA/TiO₂ in the presence of phosphate or fluoride (Figure S9b). The fluoride or phosphate modification replaces the surface hydroxyl groups with fluoride or phosphate and hinders HA adsorption/complexation onto TiO₂, indicating that light absorption should be related to complexation between TiO₂ and HA. To clarify the photosensitization mechanism responsible for the visible-light photocatalytic activity of HA/TiO₂, the dependence of the rate of 4-CP degradation on the wavelength of incident light was examined. The trend of degradation rates matched well with the LMCT absorption tail, rather than the HA absorption spectrum (inset of Figure 2b). Thus, the TiO₂/HA complex...
can induce additional light absorption at \( \lambda > 400 \text{ nm} \) via LMCT and enable enhanced visible-light photocatalytic degradation of 4-CP.

**Reaction Mechanism of HA/TiO\(_2\) in Visible Light.**

Upon visible-light irradiation, photoelectrons generated through the LMCT process are transferred to O\(_2\) to form O\(_2^{•−}\). H\(_2\)O\(_2\) can be produced by a disproportionation of HO\(_2^{•}\) (eqs 1 and 2).\(^{33,34}\)

\[ \text{O}_2 + e^{-} \rightarrow \text{O}_2^{•−} + \text{H}^+ \rightarrow \text{HO}_2^{•} \]  
\[ \text{HO}_2^{•} + \text{H}^+ + e^{-} \rightarrow \text{H}_2\text{O}_2 \]  

Figure 3a shows that only a negligible amount of O\(_2^{•−}\) was generated upon visible-light irradiation of HA/TiO\(_2\) (at a similar level to XTT control), in contrast to significant production of H\(_2\)O\(_2\). While this seems to suggest that H\(_2\)O\(_2\) is formed from O\(_2\) reduction rather than O\(_2^{•−}\) disproportionation, it may be explained by the short lifetime of O\(_2^{•−}\) under acidic conditions and HA—catalyzed O\(_2^{•−}\) decay, resulting in lower O\(_2^{•−}\) concentrations.\(^{35}\) Indeed, the typical EPR peak for the DMPO—OOH adduct was observed in Figure S10a,
demonstrating that both uncatalyzed and catalyzed \( \text{O}_2^{•−} \) decay are involved in \( \text{H}_2\text{O}_2 \) generation. The maximum production of \( \text{H}_2\text{O}_2 \) on HA/TiO\(_2\) was obtained at a HA concentration of 10 mg L\(^{-1}\) (Figure 3b), indicating that this is an optimal system-specific concentration that enables strong complexation with TiO\(_2\). To examine \( \cdot\text{OH} \) production from the decomposition of in situ-generated \( \text{H}_2\text{O}_2 \) changes in the fluorescence intensity of HPF and coumarin–OH adduct (7-hydroxycoumarin, 7-HC) were monitored. Despite much higher fluorescence signals of HPF and 7-HC in HA/TiO\(_2\) than those in TiO\(_2\) (Figure S11), the \( \cdot\text{OH} \) peaks were not confirmed in the EPR analyses of TiO\(_2\) and HA/TiO\(_2\) (Figure S10b). It is likely that \( \cdot\text{OH} \) was generated only in low concentration in the HA/TiO\(_2\) system, which is consistent with its inability to degrade DCA (Figure S1). On the other hand, if this result is attributed to \( \cdot\text{OH} \) scavenging by HA,\(^3\) the amount of \( \cdot\text{OH} \) generated should decrease as a function of HA concentration. However, a negligible influence of HA concentration (in the range of 2–20 mg/L) on \( \cdot\text{OH} \) production (Figure 3b) infers that scavenging effects were not significant. Therefore, we do not exclude the possible contribution of \( \cdot\text{OH} \) in 4-CP degradation but postulate that its contribution is small.

We also verified the role of ROS in 4-CP degradation by employing different radical scavengers, such as CAT for \( \text{H}_2\text{O}_2 \), TBA for \( \cdot\text{OH} \), and SOD for \( \text{O}_2^{•−} \) (Figure S12). Contrary to the weak quenching effect of TBA, significant inhibition was observed in the presence of CAT. Of note, the addition of SOD increased rather than inhibited the degradation, likely due to the greater contribution of \( \text{H}_2\text{O}_2 \) generated from the disproportionation of superoxide by SOD (eq 3) than \( \text{O}_2^{•−} \) quenching.

\[
2\text{O}_2^{•−} + 2\text{H}^+ + \text{SOD}_2 + \text{H}_2\text{O}_2
\]

(3)

Further evidence that in situ-generated \( \text{H}_2\text{O}_2 \) acts as a primary reactive species is provided by studies of the oxygen content-dependent degradation. The degradation of 4-CP was almost completely retarded in the \( \text{O}_2 \)-depleted condition (Ar-purged), while it was enhanced in the \( \text{O}_2 \)-saturated condition (Figure S12), a finding consistent with a linear increase in \( \text{H}_2\text{O}_2 \) production with increasing \( \text{O}_2 \) concentrations (Figure S13).

Role of the HA Functional Group. HA chemistry plays a critical role in driving LMCT complex formation with the TiO\(_2\) surface, and the functional groups −OH, −COOH, −SH, and −NH\(_2\) deserve special attention as they are representative of chemistries found in HA.\(^{37}\) Despite the high chemical heterogeneity of HA, the dominance of carboxylic and phenolic groups over amine and thiol groups is common in a wide variety of HAS.\(^{38}\) In addition, the functional groups bonded to the benzene ring vary in their electron donating capacities and subsequently influence the optical response. Thus, the relative contribution of each of these functional groups to changes in the optical property of TiO\(_2\) was investigated by systematically varying the functional group-bearing ligands such as pyrocatechol, phthalic acid, thiophenol, and aniline at equivalent doses. The DR UV–vis spectra of the organic ligand/TiO\(_2\) complexes are shown in Figure 4a, where pyrocatechol/TiO\(_2\) revealed a wide range of visible-light absorption, but very little or no absorption was observed for other complexes. Considering that neither pyrocatechol nor TiO\(_2\) responds to visible light (Figure S14), the optical response of the pyrocatechol–TiO\(_2\) complex provides further evidence that LMCT has a role in the visible-light activation of HA/TiO\(_2\) rather than conventional sensitization.

Given that \( \text{H}_2\text{O}_2 \) was the main ROS formed by visible-light-irradiated HA/TiO\(_2\), the visible-light activity of ligand/TiO\(_2\) complexes was tested for \( \text{H}_2\text{O}_2 \) production (Figure 4b). The \( \text{H}_2\text{O}_2 \) production was only evident in the pyrocatechol/TiO\(_2\) complex which showed a pronounced light harvesting capability in the visible range (Figure 4a). Furthermore, pyrocatechol/TiO\(_2\) had a higher degradation efficiency for 4-CP (Figure S15), implying that the in situ-generated \( \text{H}_2\text{O}_2 \) could be involved in the degradation of organic pollutants. Taken together, it seems that the phenolic group–complexed surface is a plausible representation of the active site for visible-light absorption and \( \text{H}_2\text{O}_2 \) production on HA/TiO\(_2\). The higher yield of \( \text{H}_2\text{O}_2 \) on HA/TiO\(_2\) compared to pyrocatechol/TiO\(_2\) might be linked to the stability of the LMCT complex.\(^3\) HA/TiO\(_2\) which would be expected to form a stable LMCT complex on TiO\(_2\) due to the presence of various anchoring groups within the HA, showed a greater magnitude of visible-light absorption than pyrocatechol/TiO\(_2\) (Figure 2b), leading to a higher \( \text{H}_2\text{O}_2 \) production at a given time. Note, however, that a different trend in \( \text{H}_2\text{O}_2 \) production was found between HA/TiO\(_2\) and pyrocatechol/TiO\(_2\). The concentration of \( \text{H}_2\text{O}_2 \) in HA/TiO\(_2\) became saturated after 90 min of irradiation, whereas in pyrocatechol/TiO\(_2\) it increased linearly upon irradiation.

The overall yield of \( \text{H}_2\text{O}_2 \) was determined by the formation and decomposition of \( \text{H}_2\text{O}_2 \) on the TiO\(_2\) surface under visible-light irradiation,\(^{39,40}\) thus, we tested photocatalytic \( \text{H}_2\text{O}_2 \) decomposition on HA/TiO\(_2\) and pyrocatechol/TiO\(_2\). \( \text{H}_2\text{O}_2 \) was photodegraded more slowly over pyrocatechol/TiO\(_2\) than in the HA/TiO\(_2\) system (Figure 4c). Indeed, when we compared the rates of \( \text{H}_2\text{O}_2 \) formation and decomposition for HA/TiO\(_2\) and pyrocatechol/TiO\(_2\), the formation rate constants were found to be similar to each other, but pyrocatechol/TiO\(_2\) exhibited a lower decomposition rate constant compared to that of HA/TiO\(_2\) (Figure 4d). These results agree with our previous findings that surface functional groups played a different role in enhancing the production of \( \text{H}_2\text{O}_2 \) via photocatalysis.\(^3\) Note that although we examine the role of pyrocatechol and other ligands in LMCT sensitization, they represent only a small fraction of the total HA functional groups.

Environmental Implications. Our results demonstrate that the complexation of DOM with the TiO\(_2\) surface leads to visible-light-driven \( \text{H}_2\text{O}_2 \) production, which would enable the degradation of organic pollutants and microbial inactivation. We also confirmed the appreciable production of \( \text{H}_2\text{O}_2 \) by the TiO\(_2\)–DOM complex in real river water under simulated sunlight (Figure 5), although the \( \text{H}_2\text{O}_2 \) yield decreased due to the presence of various anions that influence the complexation between TiO\(_2\) and DOM. It is expected that the \( \text{H}_2\text{O}_2 \) concentration generated at commonly reported low TiO\(_2\) concentrations in aquatic systems\(^{42,43}\) would be below the predicted no-effect concentration of \( \text{H}_2\text{O}_2 \) for aquatic organisms (380 nM).\(^4\) However, in certain areas affected by point sources or urban runoff, there might be relatively high TiO\(_2\) levels (e.g., 150 μg L\(^{-1}\) or higher)\(^4\) that generate harmful \( \text{H}_2\text{O}_2 \) concentrations. Furthermore, Fenton-like conversion of in situ-formed \( \text{H}_2\text{O}_2 \) to the stronger oxidant \( \cdot\text{OH} \) could occur in the presence of reduced metals (e.g., Fe(II)). Thus, further research is recommended to examine the dynamics of \( \text{H}_2\text{O}_2 \) formation and decomposition under various
water chemistry conditions and its effects on the biological activity of aquatic species.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.est.2c02975.

Schematic illustration of dye sensitization and LMCT sensitization of TiO$_2$; physicochemical characteristics of the river water sample; PL decay parameters of HA and HA/TiO$_2$; degradation of DCA under visible light; effect of TBA addition on the degradation of 4-CP under UV and visible-light irradiations; adsorption isotherm of HAs on TiO$_2$ and zeta potential of TiO$_2$ and HA as a function of pH; degradation of 4-CP and reduction of Cr(VI) under visible light at pH 6; characterization of HA/TiO$_2$; PL spectra and nanosecond resolved decay for emission maxima at 550 nm; photocatalytic degradation of HA with TiO$_2$; DR UV–vis spectra of TiO$_2$ and HA/TiO$_2$ at pH 6.6; DR UV–vis spectra and degradation of 4-CP by HA/TiO$_2$ in the presence of phosphate or fluoride under visible light; EPR spectra; photogenerated *OH detection; effects of scavengers and oxygen content on 4-CP degradation by HA/TiO$_2$; effect of dissolved oxygen concentration on the photocatalytic production of H$_2$O$_2$; UV–vis absorption spectrum of pyrocatechol; and degradation of 4-CP by organic ligand/TiO$_2$ under visible light (PDF)

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### Notes

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Dynamics.
Origin of Non-Single-Exponential and Particle Size Independent
Back Electron Transfer from TiO
Ligand-to-Metal Charge Transfer under Visible Light.


