Visible Light Sensitized Production of Hydroxyl Radicals Using Fullerol as an Electron-Transfer Mediator

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* Supporting Information

ABSTRACT: Fullerenes and their derivatives are known to photosensitize the production of singlet oxygen (\(1O_2\)), but their role in generating hydroxyl radical (\(OH\)) under visible light has not been reported. Here, we demonstrate that fullerol can mediate the electron transfer from Rhodamine B dye to \(O_2\) under visible light irradiation, achieving simultaneous dye decolorization and \(OH\)-induced degradation of 4-chlorophenol. The hydroxyl radical is proposed to be produced via a consecutive reduction of molecular oxygen by fullerol anion radical, which is formed through the electron transfer from the dye to the triplet state of fullerol. Mechanistic investigations using various probe reagents such as superoxide dismutase (superoxide quencher), t-butanol (\(OH\) quencher), and coumarin (\(OH\) probe) provided indirect evidence for the generation of \(OH\) under visible light. Furthermore, spin trapping technique directly detected the oxidizing species such as \(OH\), \(HO_2^-\), and \(1O_2\) in the visible light irradiated solution of RhB/fullerol mixture. It was proposed that the photochemical oxidation mechanism depends on pH: \(OH\) production is favored at acidic pH through fullerol-mediated sequential electron transfer while \(1O_2\) is generated as a main oxidant at neutral and alkaline condition through the energy-transfer process. Therefore, the photochemical oxidation can be switchable between \(OH\)-driven and \(1O_2\)-driven mechanism by a simple pH adjustment.

INTRODUCTION

The photosensitizing activity of \(C_{60}\) fullerenes to mediate energy and electron transfer enables the production of various reactive oxygen species (ROS) under visible light irradiation. Superoxide radical anion (\(O_2^-\)) is generated when \(C_{60}\) in Triton X100 surfactant matrix is photochemically excited in the presence of trimethylamine as an electron donor.\(^5\) Photon energy transfer from the triplet state of \(C_{60}\) derivatives to dissolved oxygen produces singlet oxygen (\(1O_2\)) in aqueous media.\(^6\)\(^7\) Whereas water-stable \(C_{60}\) aggregates exhibit insignificant photochemical properties via triplet–triplet annihilation and self-quenching mechanism,\(^5\)\(^9\) ozone-treated products of \(C_{60}\) that are introduced with the oxygen-containing functionalities on the cage structure are reported to generate ROS to inactivate Escherichia coli under black light irradiation.\(^10\)

Despite the photosensitizing activity of pristine \(C_{60}\) for ROS generation, the hydrophobicity and the extremely low solubility of pristine \(C_{60}\) in water (\(log K_{\text{sw}} = 6.67\)) limit its application for photochemical treatment of water. Thus, chemical derivatization has been attempted to make \(C_{60}\) soluble in water and to hinder its dense clustering, which significantly lowers the efficiency of \(C_{60}\) mediated energy transfer.\(^5\) Multihydroxylated fullerene (i.e., fullerol) is well soluble in water and has been demonstrated to produce \(1O_2\) for photochemical inactivation of MS-2 bacteriophage.\(^12\) A comparative study using various \(C_{60}\) derivatives demonstrated superior performance of aminofullerene in \(1O_2\)-induced decomposition of selected pharmaceutical compounds and inactivation of MS-2 phage under visible light irradiation.\(^7\) Furthermore, the recovery and recycling of fullerene-based sensitizer after photochemical treatment of organics in water are enabled by their immobilization on functionalized silica and mesoporous silica supports containing nano-sized magnetite.\(^13\)\(^14\)

Another interesting property of \(C_{60}\) derivatives is the electron-shuttling capability in photochemical redox systems, which has been rarely employed in the rational design of fullerene-based photochemical treatment processes for the following reasons. First, superoxide formed via one-electron transfer to dissolved oxygen provides a minor degradative pathway because of the mild oxidizing power \(E'(O_2^-/H_2O_2) = 0.89\) \(V_{\text{NHE}}\).\(^13\) Second, the \(C_{60}\) mediated electron transfer requires the presence of electron-donating substrates. However, organic pollutants as an electron donor may be utilized along...
with C_{60} derivatives in inducing the fullerene-mediated electron transfer for ROS production. Dye (representing a major class of recalcitrant pollutants) that readily undergoes visible light induced sensitization to donate electrons (i.e., oxidatively decolorized) is an ideal test substrate for this purpose. In such system, water-soluble C_{60} derivatives would facilitate the transfer of electrons from the visible light excited dyes to O_2, achieving concurrent dye decolorization and ROS (e.g., OH) production (see Scheme 1). A possible role of C_{60} as an electron shuttle was proposed from a study of photosensitized production of hydroperoxyl radical (HO_2) from H_2O_2 in the dye/C_{60} system in which water-soluble C_{60} clusters enable the delivery of electrons from the UV-excited dyes to H_2O_2. Other studies also found that C_{60} derivatives readily accept electrons from the excited dye sensitizers. Such previous results raise a possibility of utilizing consecutive transfer of electrons to dioxygen via C_{60} as a method to generate OH radical in the dye/C_{60} system. The production of nonselective OH that enables the oxidative degradation of a broad range of organic contaminants is essentially needed in the development of efficient advanced oxidation processes (AOPs).

In this study, we propose and attest the hypothesis that fullerol as an electron shuttle can mediate the successive reduction of dioxygen to OH via the sensitization of a dye, Rhodamine B (RhB), by monitoring the simultaneous decolorization of RhB and the decomposition of 4-chlorophenol (4-CP) under the visible light irradiation (λ > 420 nm). The effects of experimental parameters such as photoexcitation wavelengths, pH, and various probe reagents on the concurrent degradation of RhB and 4-CP were systematically investigated to understand the overall photochemical mechanisms.

**Materials and Methods**

**Chemicals and Materials.** Fullerol (C_{60}(OH))_x(ONa)_y with x + y = 24, y = 6 – 8 was purchased from MER corporation (Tucson, AZ). The chemicals used in this work were 4-chlorophenol (4-CP, Sigma), Rhodamine B (RhB, Aldrich), furfuryl alcohol (FFA, Aldrich), dichloroacetate (DCA, Aldrich), tetramethylammonium chloride (TMA, Acros), Na_2Cr_2O_7 (Cr(VI), Aldrich), tert-butanol (1-BuOH, Aldrich), hydrogen peroxide (H_2O_2, Junsei), superoxide dismutase from bovine erythrocytes (SOD, Sigma), L-histidine (Sigma), coumarin (Sigma), 5,5-dimethyl-1-pyrrroline-N-oxide (DMPO, Sci), 2,2,6,6-tetramethyl-4-piperidone (TEMPO, Aldrich), and deuterium oxide (D_2O, Aldrich). All chemicals were used as received without further purification. Ultrapure deionized water (18 MΩ·cm) was used to prepare all aqueous solutions. Argon gas purging of the aqueous solution was carried out when the absence of dissolved oxygen was needed. Mesoporous SO_2 (SBA-15, Sigma-Aldrich) with average particle size of 150 μm and average pore size of 8 nm was used for the immobilization of fullerol. The SBA-15 was dispersed in an aqueous fullerol solution (50 μM), and pH was subsequently adjusted to 3 with HClO_4. After stirring for 5 h, the fullerol/ SBA-15 was collected by filtering and was dried in an open-air oven (80 °C).

**Photochemical Experiments.** Photochemical experiments employed a 300 W Xe arc lamp (Oriel) as a light source and were performed in a 30 mL Pyrex reactor with a quartz window under air-equilibrated condition. Irradiation of visible light at an ambient temperature was achieved by passing light through a 10 cm IR water filter and a cut-off filter (λ > 420 nm). For measuring the wavelength-dependent photoactivities, a monochromator (Oriel) was used to vary the wavelength in the range of 400–640 nm. All monochromatic light intensities were measured to be 1.17 ± 0.15 mW cm⁻² using a Power meter (Newport 1918-R). A typical solution of the photosensitizing system was prepared at a concentration of 100 μM RhB, 50 μM fullerol, and 50 μM substrate (4-CP, DCA, or TMA). The experimental solution was unbuffered in most cases, and the initial pH was adjusted to a desired value with 1 M HClO_4 or NaOH solution. On the other hand, the experiments to monitor FFA (100 μM) degradation at pH 7 were conducted in aqueous solutions of RhB and fullerol, buffered with 10 mM phosphate. Aliquots of 1 mL were intermittently withdrawn from the photoirradiated reactor using a 1 mL syringe and were transferred into a 2 mL amber glass vial (without filtration). Chemical reagents to quench any oxidants that might be produced during the reaction were not used. To confirm the reproducibility, the experiments were performed at least five times for any given condition.

**Analysis.** The concentrations of 4-CP and FFA were quantitatively analyzed using a high-performance liquid chromatograph (HPLC, Agilent 1260 Infinity) equipped with a diode array detector and a ZORBAX 300SB-C18 column (4.6 mm × 150 mm). The HPLC measurement of 4-CP was carried out using binary mobile phase of 85% (v/v) aqueous phosphoric acid solution and acetonitrile (70:30 by volume), while FFA quantification was done using 40% aqueous methanol eluent. The ion chromatography (HPLC, Agilent 1260 Infinity) equipped with a diode array detector and a ZORBAX 300SB-C18 column (4.6 mm × 150 mm) for cation (TMA) analysis or AS-14 (4 mm × 250 mm) column for anion (DCA and Cl⁻) analysis. For the cation analysis, 10 mM methanesulfonic acid was used, and for the anion analysis, 3.5 mM Na_2CO_3/1 mM NaHCO_3 was used. The removal of total organic carbon (TOC) in the visible light irradiated RhB/fullerol solution was monitored using a TOC analyzer (Shimadzu TOC-V). The production of OH was indirectly monitored using coumarin as a chemical trap of OH, which is oxidatively converted into 7-hydroxycoumarin through the reaction with OH. The hydroxylated product was quantified by measuring fluorescence emission intensity at 460 nm under the excitation at 352 nm. RHB concentrations were spectrophotometrically determined by monitoring the absorbance at 554 nm (ε = 10546 DOI:10.1021/acs.est.6b03250

The solution pH was initially adjusted to 3 and the concentration of \([\text{RhB}] = 100\) μM, which was employed in this study (see Figure S1). The solution pH was initially adjusted to 3 and was marginally changed in the course of photosensitized irradiation (\(\lambda > 420\) nm) when fullerol is present. The sensitized degradation of 4-CP was maximal at the concentration of \([\text{RhB}] = 100\) μM, which was employed in this study (see Figure S1). The solution pH was initially adjusted to 3 and was marginally changed in the course of photosensitized reaction. Neither direct photolysis nor dark adsorption on fullerol removed RhB and 4-CP at all (see Figure S2). Regardless of the presence of RhB, fullerol degraded RhB under visible light (Figure 1), which indicates that fullerol oxidizes RhB molecules as suggested in Scheme 1. Where the use of fullerol alone slightly degraded 4-CP through a direct electron transfer from 4-CP to \(3\text{C}_{60}(\text{OH})_x^*\) (i.e., 4-CP + \(3\text{C}_{60}(\text{OH})_x^* \rightarrow 4\text{-CP}^* + \text{C}_{60}(\text{OH})_x^*\)) under visible light irradiation, the degradation of 4-CP was significantly enhanced in the binary RhB/fullerol system. Some quinone compounds (e.g., benzoquinone (BQ), catechol (CC), hydroquinone (HO), hydroxyhydroquinone (HHQ)) were detected as hydroxylated intermediates during the photosensitized degradation of 4-CP in the RhB/fullerol system (Figure S3a). However, such hydroxylated products of 4-CP degradation were not observed when fullerol alone was used as the sensitizer (Figure S3b). This implies that the interaction between excited fullerol and RhB molecules induces the production of OH (Scheme 1). OH-induced oxidation of chlorophenols leads to the generation of chloride and other intermediates via multiple reaction pathways (1) OH addition to the aromatic ring of chlorophenol to yield chlorodihydroxydihydroxybenzyl (CDHCHD) radical, (2) the addition of \(\text{O}_2\) to CDHCHD radical or the coupling and disproportionate of two CDHCHD radicals, and (3) the subsequent rearrangement to release a chloride ion with the formation of various intermediates (e.g., hydroquinone and catechol).

Figure 2 compares the efficiencies of the RhB/fullerol system for RhB decolorization and 4-CP degradation as a function of the irradiation wavelength that was controlled by a monochromator. The removal efficiencies of both RhB and 4-CP were the highest at 550 nm, which is in agreement with the absorption maximum of RhB spectrum. This indicates that the sensitization by RhB is important in the overall photochemical process. The photoexcited RhB can donate electrons to excited and ground states of \(\text{C}_{60}(\text{OH})_x\) under visible light. However, the photodegradation activities of RhB and 4-CP are also significant even at the wavelengths where RhB hardly absorbs (i.e., 400–460 nm region). This implies that not only the excited RhB but also the excited fullerol contributes to the overall photodegradation process as Scheme 1 shows. The comparison of reduction potentials \(E^\prime(\text{C}_{60}(\text{OH})_x^*) = +1.10\)
\( V_{\text{NHE}} \) vs. \( E^0(\text{C}_{60}(\text{OH})_x) = -0.20 \ V_{\text{NHE}} \)\(^{16} \) implies that \(^3\text{C}_{60}(\text{OH})_x^* \) is a stronger oxidant than its ground state.

**Reaction Mechanisms.** Photochemical degradation of 4-CP in the RhB/fullerol solution was tested under argon-saturated condition where the oxidant generation via O\(_2\) reduction should not be possible. Very slow 4-CP decomposition occurred in the absence of O\(_2\) (Figure 3a). The addition of chromate (i.e., Cr(VI)) as an alternative electron acceptor in the presence of dissolved O\(_2\) also induced a marked retardation in the rate of 4-CP degradation (Figure 3a), which is attributable to the competition between chromate and 4-CP to react through the excited triplet states of sensitizer such as porphyrin\(^22\) and humic\(^23\) substances supports the nonradical mechanism involving \(^3\text{C}_{60}(\text{OH})_x^* \).

The transformation of dioxygen into hydroxyl radical may involve the production of H\(_2\)O\(_2\) as an intermediate. Since the analysis of H\(_2\)O\(_2\) by a common colorimetric method is not possible in the presence of RhB dye, we investigated the effect of H\(_2\)O\(_2\) addition, which accelerated 4-CP degradation in the RhB/fullerol system, with \( k = 0.86 \ \text{h}^{-1} \) (with H\(_2\)O\(_2\)) vs. \( k = 0.41 \ \text{h}^{-1} \) (without H\(_2\)O\(_2\)) (Figure 3a). This supports the possibility of H\(_2\)O\(_2\) involvement as a nonradical intermediate during the successive O\(_2\) reduction into \( \cdot \text{OH} \). On the other hand, the presence of excess t-BuOH as a hydroxyl radical scavenger decelerated the photosensitized degradation of 4-CP [\( k = 0.20 \ (\pm 0.03) \ \text{h}^{-1} \) (with t-BuOH)] (Figure 3a), which supports the visible light induced production of \( \cdot \text{OH} \) in the RhB/fullerol solution. However, the fact that the addition of 0.1 M t-BuOH did not completely inhibit the 4-CP degradation implies that the direct electron transfer from 4-CP to \(^3\text{C}_{60}(\text{OH})_x^* \) may contribute as an alternative oxidative degradation pathway (see the slight removal of 4-CP by fullerol alone (Figure 1)).\(^{24,25}\) RhB decolorization was not retarded at all when t-BuOH was added (Figure S4), which suggests that RhB is oxidized predominantly via a direct electron transfer to \(^3\text{C}_{60}(\text{OH})_x^* \).

The RhB/fullerol system was also examined for the degradation of DCA and TMA that are not reactive with O\(_2\). In particular, TMA that is very recalcitrant against oxidative degradation can be degraded only by a strong oxidant like \( \cdot \text{OH} \).\(^{26}\) Significant decomposition of DCA and TMA proceeded only in the mixture of RhB and fullerol (Figure S5) and was markedly decelerated in the presence of t-BuOH. Significant TOC reduction was not observed in any binary mixture (e.g., RhB/fullerol, 4-CP/fullerol, or RhB/4-CP) and only the ternary mixture, RhB/fullerol/4-CP, achieved the TOC removal of 19.7 mg/L after 4 h visible light irradiation (Figure 3b), which is likely attributed to \( \cdot \text{OH} \)-induced mineralization of 4-CP.

To further corroborate the possible production of \( \cdot \text{OH} \) in the RhB/fullerol system, we monitored the formation of TMA and DCA (Figure 4a) in the RhB/fullerol system. The formation of TMA arises from the reactions of the hydroxylated RhB (Figure 4a), which quenches superoxide (an intermediate to \( \cdot \text{OH} \)) and decreases the rate of 4-CP degradation, whereas \( \cdot \text{OH} \) caused no retardation in RhB decoloration (Figure 4b).

**Addition of Chromate (Cr(VI)) as an Alternative Electron Acceptor.** The electron exchange between excited and ground states of RhB and C\(_{60}(\text{OH})_x \) would result in the formation of a pair of radical cation and anion, RhB\(^+\) and C\(_{60}(\text{OH})_x^-\) (eqs 2–4), which likely occurs in parallel with one-electron oxidation of coumarin by \(^3\text{C}_{60}(\text{OH})_x^* \) in which the resulting coumarin radical cation reacts with water molecule to generate the hydroxylated product. The addition of superoxide dismutase (SOD), which quenches superoxide (an intermediate to \( \cdot \text{OH} \)), significantly reduced the efficiency of 7-hydroxycoumarin generation (Figure 4a).

Equation 1: the formation of 7-hydroxycoumarin (eq 1) as a result of hydroxylation of coumarin (a probe of \( \cdot \text{OH} \)) in the visible light irradiated solution containing RhB and fullerol.

\begin{equation}
\cdot \text{OH} + \text{coumarin} \rightarrow 7\text{-hydroxycoumarin} \tag{1}
\end{equation}

Figure 4a shows that the production of 7-hydroxycoumarin proceeded 6-fold faster in the binary RhB/fullerol solution than in the presence of fullerol alone, which also indicates the involvement of \( \cdot \text{OH} \) as a major oxidant in 4-CP decomposition. The experimental conditions that inhibit the reductive conversion of O\(_2\) (i.e., Ar-saturation, chromate (Cr(VI)) addition) significantly reduced the efficiency of 7-hydroxycoumarin generation (Figure 4a). The fact that the 7-hydroxycoumarin emission signal was not completely quenched in the Ar-saturated condition might be ascribed to a minor path of direct one-electron oxidation of coumarin by \(^3\text{C}_{60}(\text{OH})_x^* \) in which the resulting coumarin radical cation reacts with water molecule to generate the hydroxylated product. The addition of superoxide dismutase (SOD), which quenches superoxide (an intermediate to \( \cdot \text{OH} \)), decreased the rate of 4-CP degradation, whereas \( \cdot \text{OH} \) caused no retardation in RhB decoloration (Figure 4b).

Taken together, concomitant decolorization of RhB and oxidative degradation of organics (eq, 4-CP, DCA, and TMA) proceed via multiple reaction pathways as follows. The electron exchange between excited and ground states of RhB and C\(_{60}(\text{OH})_x \) would result in the formation of a pair of radical cation and anion, RhB\(^+\) and C\(_{60}(\text{OH})_x^-\) (eqs 2–4), which likely occurs in parallel with one-electron oxidation of 4-CP by \(^3\text{C}_{60}(\text{OH})_x^* \) (eq 5). The reaction route involving no ROS is based on the oxidizing power of \(^3\text{C}_{60}(\text{OH})_x^* \) (eq 5).

\begin{equation}
\cdot \text{OH} + \text{coumarin} \rightarrow 7\text{-hydroxycoumarin} \tag{1}
\end{equation}

\begin{equation}
\text{RhB}^+ + \text{C}_{60}(\text{OH})_x^- \rightarrow \text{RhB}^+ + \text{C}_{60}(\text{OH})_x^- \tag{2}
\end{equation}
Figure 4. (a) Visible light induced production of 7-hydroxycoumarin as a coumarin–OH adduct (monitored by its photoluminescence) in the aqueous solutions of fullerol, RhB, and RhB/fullerol mixture in various conditions. (b) Simultaneous degradation of RhB and 4-CP in aqueous fullerol solutions in the absence and presence of SOD ([fullerol]₀ = 50 μM; [RhB]₀ = 100 μM; [4-CP]₀ = 50 μM; [coumarin]₀ = 1 mM; [Cr(VI)]₀ = 100 μM; [SOD]₀ = 66.7 mg L⁻¹; pH₀ = 3.0; air-equilibrated except for the Ar-saturated case).

\[
\text{RhB}^+ + 3\text{C}_{60}(\text{OH})_{x}^* \rightarrow \text{RhB}^+ + \text{C}_{60}(\text{OH})_{x}^- \quad (3)
\]

\[
\text{RhB} + 3\text{C}_{60}(\text{OH})_{x}^* \rightarrow \text{RhB}^+ + \text{C}_{60}(\text{OH})_{x}^- \quad (4)
\]

\[
4\text{CP} + 3\text{C}_{60}(\text{OH})_{x}^* \rightarrow \text{C}_{60}(\text{OH})_{x}^- + 4\text{CP}^* \quad (5)
\]

\(3\text{C}_{60}(\text{OH})_{x}^*\) contributes to the production of ROS in two ways energy transfer versus electron transfer. The energy transfer from \(3\text{C}_{60}(\text{OH})_{x}^*\) to dissolved oxygen leads to the formation of \(\text{O}_2\) \((\text{eq} \ 6)\). Alternatively, the oxidative power of \(3\text{C}_{60}(\text{OH})_{x}^*\) to abstract electrons from either RhB or 4-CP enables the generation of \(\text{C}_{60}(\text{OH})_{x}^-\), which initiates the consecutive reduction of \(\text{O}_2\) for the production of \(\text{OH}\) via \(\text{O}_2^-\) \((\text{eq} \ 7)\).

\[
3\text{C}_{60}(\text{OH})_{x}^* + 3\text{O}_2 \rightarrow \text{C}_{60}(\text{OH})_{x}^- + 3\text{O}_2^- \quad (\text{1O}_2 \text{formation})
\]

\[
\text{C}_{60}(\text{OH})_{x}^* + \text{O}_2 \rightarrow \text{C}_{60}(\text{OH})_{x}^- + \text{O}_2^- \quad (\text{oxidizing radical formation})
\]

pH-Dependent Reaction Mechanism. Figure 5a shows the rates of degradation of 4-CP and furfuryl alcohol (FFA) \((\text{as } 1\text{O}_2 \text{ indicator})\) in the RhB/fullerol solution as a function of initial pH. Whereas the photosensitizing activity for FFA decomposition remained relatively constant irrespective of pH, the efficiencies for RhB decolorization and 4-CP degradation drastically decreased with increasing pH. The different pH dependence of the photochemical degradation kinetics may be attributable to switching of the reaction pathway in response to pH change: singlet oxygenation versus \(\text{OH}\)-induced oxidation. A significant reduction in the RhB and 4-CP decomposition occurred as the pH increased from 3 to 5, and further increase to pH 7 and pH 9 caused the negligible removal of RhB and 4-CP \((\text{Figure} \ 5a)\). This pH-dependent behavior indicates that the production of \(\text{OH}\) is highly favored at acidic condition. Fullerol \((\text{pK}_a = 4.0)\) carries negative charges at neutral and alkaline condition, which makes the photoinduced electron transfer from the excited dye to negatively charged fullerol \((\text{eq} \ 1)\) less favored at higher pH because of the electrostatic repulsion. In addition, the production of \(\text{OH}\) through the consecutive reduction of \(\text{O}_2\) should be favored under proton-rich condition \((\text{acidic pH})\) \((\text{see eq} \ 8)\). As a result, the hydroxyl radical-mediated mechanism should be dominant at acidic pH and less favored at alkaline condition.

\[
\text{O}_2 + 3\text{e}^- + 3\text{H}^+ \rightarrow \text{OH} + \text{H}_2\text{O}
\]

On the other hand, \(1\text{O}_2\) production via energy transfer from \(3\text{C}_{60}(\text{OH})_{x}^*\) to \(\text{O}_2\) \((\text{eq} \ 6)\) should be little affected by pH change, which caused FFA oxidation efficiency to be relatively independent of pH.

We monitored the photoluminescence (PL) intensity of the RhB/fullerol mixture as a function of initial pH \((\text{Figure} \ 5b)\). Whereas the PL intensity of RhB \((\text{in the absence of fullerol})\) remained invariant irrespective of initial pH \((\text{pH} 3 \text{ vs} \ 7)\), the PL intensity of the RhB/fullerol mixture was markedly reduced when pH decreased from 7 to 3. Considering that the electron
transfer from RhB* should lower the PL intensity, the lower PL intensity at acidic pH in the RhB/fullerol solution implies that the electron transfer from RhB* to fullerol is favored at acidic pH. This is also consistent with the higher photo degradation activity at acidic pH (Figure 5a). Acidic condition favors the direct electron transfer from RhB* to fullerol (leading to OH production), whereas it is not favored in the basic pH region.

To further characterize the production of 1O2 under varying pH condition, we performed the photochemical degradation of FFA in the solution of fullerol alone (Figure 6a) and RhB/

fullerol (Figure 6b) in the presence of t-BuOH or L-histidine (as 1O2 scavenger)26,29 at acidic and neutral pH region. Regardless of the initial pH, the addition of L-histidine caused a drastic decrease in FFA degradation efficiency in fullerol alone solution, while no such marked retardation was observed with the addition of t-BuOH (Figure 6a). This confirms that 1O2 (generated via eq 6) works as a main oxidant in the fullerol-sensitized system. When a binary mixture of RhB and fullerol was used as the photosensitizing system, the effects of L-histidine and t-BuOH were similar to Figure 6a at pH 7 but were reversed at pH 3 (Figure 6b). t-BuOH showed a much more pronounced quenching effect at pH 3 than L-histidine, which suggests that FFA was oxidized mainly by nonselective OH in the binary RhB/fullerol system at pH 3. On the other hand, the presence of L-histidine almost completely inhibited FFA decomposition at pH 7, whereas FFA was still significantly degraded when t-BuOH was added instead. This implies a role of 1O2 as a dominant oxidant in the RhB/FFA system at neutral pH. This could be further verified by comparing FFA degradation rates in deuterated water (Figure S6). At neutral pH condition where 1O2 acts as a major oxidant in the RhB/fullerol solution, the alternative use of D2O solvent that is less efficient in 1O2 deactivation (i.e., kD(O-D)= 1.6 × 10^6 s^-1; kD(H2O)= 2.4 × 10^6 s^-1)30 accelerated the rate of FFA decomposition, with k = 1.87 h^-1 in D2O versus k = 0.42 h^-1 in H2O.

Using EPR spin-trapping technique, we detected oxidizing radicals such as OH and HO2 (hydroperoxyl radical) and 1O2 in the RhB/fullerol solution, which is shown in Figure 7. The peaks characteristic of DMPO-OH and DMPO-OOH in the EPR spectra ensure that successive electron transfers from C60(OH)* to dioxygen result in the formation of OH via O2− (eq 7) at acidic condition (pH 3). In particular, when SOD as a superoxide quencher was added to the RhB/fullerol solution, the peak intensities corresponding to HO2 and OH were significantly reduced. This confirms that HO2− (or O2−) is a critical intermediate to OH formation and is consistent with the finding that 4-CP degradation was inhibited in the presence of SOD (Figure 4b). The signals for TEMP−-1O2 adducts shown in Figure 7b also confirm the sensitized production of 1O2 at pH 7. They were observed even in the absence of RhB, which assures that the singlet oxygen is generated by the sensitization of fullerol alone as illustrated in Scheme 1.

Overall, all the earlier pH-dependent results corroborate that fullerol mediates the electron transfer to accelerate the photosensitized production of OH in the presence of RhB preferably at acidic condition and enhances the energy transfer to generate 1O2 in the absence of RhB dominantly at neutral condition.

Immobilized Fullerol and System Stability. C60 derivatives were immobilized on the surface of functionalized and mesoporous silica supports to prevent their aggregation and to recycle them after photochemical reaction.31 The surface
of C60 derivatives and solid supports should be modified by various chemical functional groups such as amine\(^3\) and carboxylic acid\(^3\) for stable immobilization. However, fullerol can be easily immobilized on the surface of mesoporous silica through a hydroxyl group without further chemical treatments (Figure 8a). Figure 8b shows that concomitant degradation of RhB and 4-CP was pronounced using fullerol-loaded SBA-15 (fullerol/SBA-15) under visible light irradiation, while the use of bare SBA-15 did not cause any removal of RhB or 4-CP. Neither RhB nor 4-CP was adsorbed on fullerol/SBA-15 in the dark condition, and the addition of 4-CP did not change the absorption spectrum of fullerol/SBA-15 at all, which confirms little interaction between 4-CP and fullerol/SBA-15 (Figure S7). The heterogeneous photocatalytic activity of fullerol/SBA-15 was comparable to that of the homogeneous counterpart.

The photosensitizing activity of aqueous fullerol and fullerol/SBA-15 was evaluated by carrying out repeated cycles of 4-CP degradation and RhB decolorization in the same batch of the reactor (Figure S9). Fulleralloimmobilized on SBA-15 showed stronger stability and better performance than water-soluble fullerol during the repeated uses. Although both heterogeneous and homogeneous systems underwent gradual loss of photosensitizing activity during the multiple uses, the fullerol/SBA-15 showed 25% activity reduction whereas water-soluble fullerol exhibited 45% reduction after five cycles under the same reaction conditions. This deactivation seems to be largely caused by the gradual loss of fullerol by samplings and the gradual accumulation of substrates (4-CP and RhB) and their degradation intermediates. Although a partial deactivation of fullerol cannot be ruled out, the activity of fullerol is largely maintained throughout multiple cycles.

Environmental Applications. This study demonstrates the first instance of visible light sensitized production of \(\text{OH}\) as a result of fullerol-mediated electron transfer from the photoexcited dye to dissolved oxygen. Such \(\text{OH}\)-producing mechanism enables the degradation and mineralization of recalcitrant compounds such as 4-CP, DCA, and TMA under visible light irradiation, which is not possible with the \(\text{1O}_2\)-based mechanism that most fullerene-based photochemical oxidation systems follow. The proposed photosensitizing process achieves dye decoloration and pollutant mineralization simultaneously. The results imply that fullerol (or fullerene derivatives) may work similarly to produce \(\text{OH}\) through mediating electron transfer in the presence of natural organic matters as a photosensitizer. Such a possibility needs to be tested in further studies. Other combinations of dyes and sensitizers with fullerene derivatives also need to be investigated to test the general applicability of the proposed concept. The photo-oxidation mechanism depending on \(\text{pH}\) is an advantage since the main working oxidant can be switchable between \(\text{1O}_2\) and \(\text{OH}\). The selective \(\text{1O}_2\) undergoes limited quenching by background organic matters,\(^3\) while \(\text{OH}\) with strong oxidizing power enables the degradation of a broad range of organic compounds.\(^3\)

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b03250.
Optimization of RhB concentration for visible light activity (Figure S1), direct photolysis under visible light and dark control data (Figure S2), intermediates produced from 4-CP degradation (Figure S3), effect of t-BuOH addition on the photosensitized degradation of RhB (Figure S4), photodegradation of DCA and TMA in the RhB/fullerol solution (Figure S5), photosensitized oxidation of FFA in D2O (Figure S6), dark reaction of fullerol/ SBA-15 and absorption spectra of fullerol/ SBA-15 before and after 4-CP adsorption (Figure S7), repeated cycles of 4-CP and RhB photodegradation in the presence of aqueous fullerol and fullerol/ SBA-15 (Figure S8). 

REFERENCES


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