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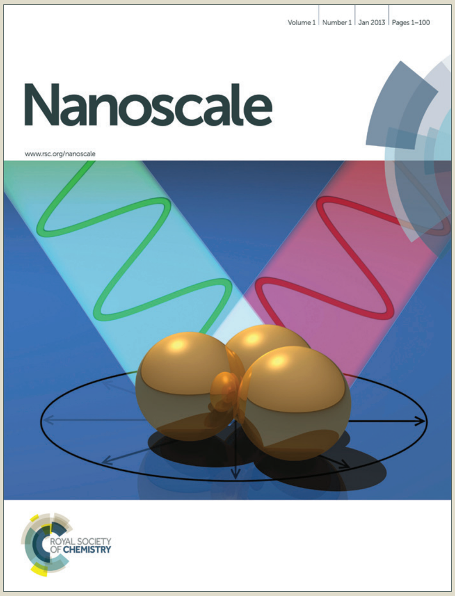

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Electron Transfer Mediation by Aqueous C_{60} Aggregates in H_2O_2/UV Advanced Oxidation of Indigo Carmine

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Abstract

C_{60} fullerene has long been known to exhibit favorable electron accepting and shuttling properties, but little is known about the possibility of electron transfer mediation by fullerene aggregates (nC_{60}) in water. In this study, we investigated the electron shuttling capabilities of nC_{60} using UV/H_2O_2 as a model oxidation process in the presence of an electron donor, indigo carmine (IC). nC_{60} addition to the IC/H_2O_2 system was found to drastically increase IC degradation and shift the reactive oxygen species (ROS) balance, favoring the formation of superoxide and perhydroxyl radical species compared to hydroxyl radicals. Results indicate that nC_{60} can act as an electron mediator, where adsorbed IC donates an electron to nC_{60}, which is subsequently transferred to H_2O_2 or perhydroxy radical.

Keywords: nC_{60}; fullerene; electron transfer; ROS; hydrogen peroxide

1. Introduction

C_{60} fullerene has been the cornerstone of many nanomaterials application due to its unique electronic and photochemical properties.[1] C_{60} is an excellent electron acceptor and can accept up to six electrons due to its relatively low-energy LUMO and the state's high degeneracy.[2] Upon visible and UV irradiation, C_{60} is readily excited to a singlet excited state ($^1C_{60}$*) and undergoes efficient intersystem crossing to produce a triplet excited state C_{60} ($^3C_{60}$*) which is an even more efficient electron acceptor (E^0= +1.1 V vs NHE) than ground state C_{60} (−0.2 V vs NHE).[3] Excited state C_{60} is also known to efficiently sensitize ground-state triplet oxygen to generate $^1O_2$, a selective oxidant useful in applications such as photodynamic therapy[4] and photocatalysis for water treatment.[5, 6] Once reduced, fullerene can transfer electrons to O_2 forming superoxide radical anion ($E^0(O_2/O_2^{\bullet-})$= −0.33 V_{NHE}) or to other terminal electron acceptors and conducting materials, serving as an efficient electron shuttle.

Fullerene's capability to mediate electron transfer has been instrumental in various applications. There have been numerous reports on the enhancement of photoactivity of semiconductor-based photocatalysts, including TiO_2, CdS/TiO_2, and Bi_2WO_6, upon surface loading of C_{60}, leading to improved reactive oxygen species (ROS) production in water.[7-11] For example, addition of fullerene resulted in improved degradation of methylene blue, methylene orange, rhodamine B, and eosin Y by semiconductors, which has been attributed to greater hydroxyl and superoxide radical production.[7, 9, 10] In these reports, it was postulated that fullerene improves ROS production by enhancing electron-hole dissociation due to electron transfer from the photocatalysts' conduction band to fullerene, which has superb electron affinity, and subsequent transfer to terminal electron acceptors such as oxygen.[12] In fact, fullerene is often used as the electron acceptor in organic photovoltaics for this very reason, i.e., to elicit dissociation of the exciton from the organic donor molecule.[13]

Upon entry into the aqueous phase, however, fullerene molecules cluster together due to their hydrophobic nature and form nanoscale aggregates with diameters of 50-250 nm, often referred to as nC_{60}.[14] Many studies have reported on the physiochemical, photochemical, and transport properties of nC_{60} in aqueous systems, an important facet of understanding the fate of fullerene in the natural environment.[15-17] Interestingly, C_{60} appears to lose much of its photochemical properties upon aggregation, as evidenced by less than pico-second lifetime of

$^3C_{60}$* in nC_{60} as compared to hundreds of micro-second lifetime in C_{60} dispersed as an individual molecule in organic solvents.[18, 19] This significant reduction in $^3C_{60}$* lifetime has been attributed to rapid quenching of C_{60} excited states by neighboring fullerene molecules at either ground state (self-quenching) or excited state (triplet-triplet annihilation), which have been brought into closer contact through aggregation.[18, 19] Despite significantly faster loss of key intermediate species, there exists experimental evidence on the photochemical production of a small amount of $^1O_2$ under certain conditions by nC_{60}.[17, 20]

Similarly, it was demonstrated that the lifetime of $C_{60}^{\bullet -}$ is also significantly reduced upon spontaneous aggregation in water, from 0.3 ms with C_{60} in surfactant micelles to below the detection limit of nanosecond scale.[18, 19] Consistently, facile formation of $O_2^{\bullet -}$ in the presence of organic electron donor by nC_{60} has not been observed.[18] However, for the same reason that the $^1O_2$ production by nC_{60} cannot be completely excluded, it might be still possible that C_{60} mediates electron transfer under certain conditions even when it forms aqueous aggregates. In fact, it has been shown that nC_{60} accepts hydrated electrons (e_{aq}^-) with diffusion-limited kinetics,[21] although the hydrated electron is one of the most powerful reductants and therefore not representative of environmentally relevant scenarios.

To further provide insight into the redox properties of nC_{60} in water, herein we investigated the role of nC_{60}'s potential electron transfer mediation on the oxidation of a model dye, indigo carmine (IC). Based on the fact that nC_{60} still retains some photoactivity in water, we postulate that C_{60}'s redox properties might be preserved upon aggregation and that reduction of nC_{60} in water is possible, albeit at possibly diminished levels. We tested this hypothesis using the UV/H_2O_2 system, the most widely used advanced oxidation process in water treatment, and examined the effect of nC_{60} on IC degradation rates. Using this system, an increase in IC oxidation would indicate the role of nC_{60} as an electron shuttle. Results presented herein provide a strong indication that nC_{60} possesses some reduction capabilities, although only in acidic environment.

2. Materials and methods

2.1. Chemicals

Chemicals used in this study include: IC, H_2O_2 (30% w/w), dimethyl sulfoxide (DMSO), potassium titanium (IV) oxalate (reagent grade, Sinopharm Chemical Reagent Co., Ltd, China), 5,5-dimethyl-1-pyrroline N-oxide (DMPO) (Sigma-Aldrich, USA), superoxide dismutase (SOD), catalase (CAT) (Worthington Biochemical Corp., USA), terephthalicacid (TA), nitro blue tetrazolium (NBT) (Urchem Corp, China), C_{60} (99.9%, MER Corp., USA), and toluene (HPLC grade, Merck KGaA, Germany). All chemicals were used as received. Reaction solutions were prepared using ultrapure water (18.2 MΩ/cm) produced by a water filtration system (HITACHI, Japan) and buffered using phosphate.

2.2. nC_{60} Preparation

nC_{60} suspensions were prepared by a solvent exchange method using toluene and ultrapure water according to previous report.[22] Briefly, 40 mg of dry C_{60} powder was dissolved in 100 mL of toluene and shaken in a sealed bottle overnight in order to completely dissolve C_{60}. Ultrapure water (400 mL) was added and ultrasound at 80 W was applied to transfer C_{60} from toluene into the aqueous phase for 48 h. Toluene was subsequently evaporated using a rotary evaporator (Buchi Rotavapor System, Switzerland) and the aqueous solution was filtered through a 0.22 μm nylon syringe membrane, producing a transparent brown-yellow colored suspension. nC_{60} particle sizes and zeta potentials were determined before and after photoreactions using multi-angle light scattering coupled with asymmetric flow field flow fractionation (AF4, Wyatt Technology Corporation, USA) and electrophoretic light scattering (Delsa 7M Nano C, USA), respectively; detailed experimental methods are described in Supporting Information.

2.3. Batch experiments

Batch photochemical experiments were carried out in a quartz cylindrical reactor, which was placed 10 cm from the light source. Six black light blue lamps (365 nm, BLB lamps, Philips TL8W) were used as the light source, providing an average intensity of 0.72 mW/cm^2 as measured by a radiometer (FZ-A Photoelectric Instrument Factory, Beijing Normal University, China). A typical reaction solution was composed of 2.2 mM H_2O_2, 10 mM phosphate, 125 μM IC and varying concentrations of nC_{60} aggregates. Solution pH was adjusted using 0.05 M NaOH or HCl. Aliquots of the reactor solution (1 mL) were withdrawn from the reactor at given time points and the absorbance of IC was measured at 620 nm via a UV-Vis spectrophotometer (UV-1800, MAPADA, China). Concentration of H_2O_2 was determined by adding 3 mL of potassium titanium (IV) oxalate (10 mM in 2.4 M H_2SO_4) which forms an orange complex (pertitanic acid) with maximum absorption at 400 nm.[23] The samples were allowed to develop for 10 min before the solution's absorbance was measured via UV-vis spectroscopy. Dark controls were conducted by wrapping the cylinders using an aluminum foil. All the batch experiments were performed three times at room temperature (25 °C).

2.4. Hydroxyl and superoxide radical analysis

$^{\bullet}OH$ production was determined via a terephthalic acid (TA) fluorescence probe method.[24] The reaction medium contained 4 mM TA and sample aliquots were analyzed using a fluorescence spectrophotometer (Shimadzu RF-5300PC, Japan; $\lambda_{max,ex}$=312 nm; $\lambda_{max,em}$=425 nm). NBT (0.1 mM) was used as an indicator for the production of $O_2^{\bullet -}$ in the presence of triethylamine (TEA, 8 mM) as an electron donor. For electron paramagnetic resonance (EPR) analysis, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 0.37 M) was added to the reaction solution as a spin-trapping agent. The photochemical reactions were performed following the same procedure described above and the sample aliquots were analyzed using a JES FA 200 EPR spectrometer (JEOL Corp., Japan) under the following conditions: temperature = 296 K, microwave power = 1 mW, modulation width = 0.1 mT, modulation frequency = 100 kHz, center field = 323.3 mT.

3. Results and discussion

3.1. IC Degradation

The effect of nC_{60} on IC degradation by H_2O_2 under UVA irradiation and in the dark at pH 3 is depicted in Fig. 1. The structure and absorption spectrum of IC is shown in Fig. S1. The oxidation of IC causes opening of C=C double bond, leading to decoloration of IC solution due to loss of conjugation center. IC did not exhibit significant photodegradation under UVA illumination in the absence of H_2O_2 or nC_{60}. Upon addition of nC_{60}, IC degradation increased slightly, which may be attributed to reaction with small amounts of $^1O_2$ photosensitized by nC_{60} or by IC adsorption onto nC_{60}.[20, 25] Under the dark condition, it appears that a small amount of IC was also lost with only nC_{60} present, suggesting that some of the IC adsorbed to nC_{60}. IC degradation increased drastically upon addition of H_2O_2. H_2O_2 is known to be a mild oxidant (E^0= +1.78 V vs NHE) and can directly react with IC or undergo photolysis, producing $^{\bullet}OH$ that oxidizes IC. Note that the IC degradation rate was substantially slower in the dark condition, suggesting that excited IC might contribute to faster degradation kinetics or $^{\bullet}OH$ production from H_2O_2 was enhanced upon light irradiation. In UV/H_2O_2 advanced oxidation processes, medium or low pressure mercury lamps provide photons that photolyze H_2O_2, producing $^{\bullet}OH$.[26, 27] Generally, UVC irradiation is used to excite H_2O_2 and lead to decomposition; however, H_2O_2 photolysis and $^{\bullet}OH$ production have been also observed under UVA illumination in a few reports.[28, 29] IC degradation was further increased upon addition of nC_{60} with H_2O_2 and exhibited a dose dependent response for both light and dark conditions. The IC degradation rate was significantly faster under UV illumination compared to the dark condition, suggesting that light played a critical role in the IC degradation process. However, it is noteworthy that nC_{60} appeared to increase the degradation of IC even in the dark. Through these photochemical experiments, nC_{60} remained unaffected as evidenced by no measurable change in particle size before and after photoreaction and no significant change in total number as calculated by ASTRA V software (Fig. S2).

However, nC_{60} addition to the IC/H_2O_2 system appeared to no longer increase IC degradation as the solution pH was increased above 5. Fig. 2 depicts the overall trend of increased IC degradation as pH decreases. pK_a of IC is 12.2 and therefore acid/base speciation of IC does not account for this pH dependence. One key reactive species that may be formed in the IC/H_2O_2 system is $O_2^{\bullet -}$, which exists in equilibrium with the perhydroxy radical ($HO_2^{\bullet}$) according to $O_2^{\bullet -} + H^+ \leftrightarrow HO_2^{\bullet}$ with pK_a=4.8. Therefore, at pH below 4.8, the dominant form is the $HO_2^{\bullet}$, while at pH above 4.8 the dominant form is $O_2^{\bullet -}$. Considering that the $HO_2^{\bullet}$ is a potent oxidant, whereas $O_2^{\bullet -}$ is a weak reductant,[30] it is likely that IC possibly reacts more readily with $HO_2^{\bullet}$ than $O_2^{\bullet -}$ leading to increased IC degradation at low pHs. Many studies have attributed the *in vivo* toxicity of superoxide species to the $HO_2^{\bullet}$ even though only small amounts are present at physiological pHs.[31, 32] This difference in reactivity between $O_2^{\bullet -}$ and its conjugate acid may explain the observed trend in IC degradation as a function of pH and suggests that $HO_2^{\bullet}$ may be one of the main species responsible for IC degradation.

3.2. H_2O_2 Consumption

Fig. 3 depicts the consumption of H_2O_2 as a function of time in various solutions containing IC, H_2O_2 and/or nC_{60}. The solution containing only IC and H_2O_2 did not exhibit significant H_2O_2

consumption. However, upon addition of nC_{60}, H_2O_2 consumption increased in a dose-dependent manner, suggesting that nC_{60} may play some role in the catalytic decomposition of H_2O_2. At point **a** in the graph, IC was completely decolorized and H_2O_2 consumption did not readily occur until additional IC was added to the solution at point **b**. This result suggests that IC is necessary for H_2O_2 decomposition by nC_{60} and that nC_{60} does not consume H_2O_2 by itself. That is, nC_{60} does not solely act as a catalytic surface to mediate the decomposition of H_2O_2. Furthermore, oxidation of nC_{60} by H_2O_2 did not likely occur, as no changes in nC_{60} were observed as discussed above. From this H_2O_2 consumption data, it is clear that IC, H_2O_2, and nC_{60} must all be present to induce significant H_2O_2 decomposition.

3.3. ROS Identification

Fig. 4 shows the results of EPR spectroscopy analysis when the solution containing IC, H_2O_2, and nC_{60} were illuminated with UVA light. In solutions of IC and nC_{60}, no DMPO spin adducts were apparent, suggesting that ROS was not readily produced. UV irradiation of IC and H_2O_2 solution produces a prominent 1:2:2:1 quartet signal arising from the hydroxyl adduct of DMPO, DMPO-OH ($a_N = a^{\beta}_H = 1.48$ mT).[33] In the presence of methanol, the EPR spectrum exhibited a small sextet signal originating from DMPO-superoxide adduct, DMPO-OOH ($a_N =$ 1.37 $a^{\beta}_H = 1.09$, $a^{\alpha}_H = 0.10$ mT).[34] This EPR signal suggests that both $^{\bullet}OH$ and $O_2^{\bullet-}$ are created in the IC/H_2O_2 system. Upon addition of nC_{60} to the IC/H_2O_2 system, the EPR signal of DMPO-OOH· adduct increased and signal of DMPO-OH· adduct decreased. This result suggests that nC_{60} may encourage $O_2^{\bullet-}$ production and deter $^{\bullet}OH$ formation through some yet unknown mechanism. Addition of catalase and DMSO, scavengers of H_2O_2 and ·OH, respectively, to the nC_{60}+IC/H_2O_2 system resulted in the complete disappearance of DMPO-OH· and DMPO-OOH· adduct signals, suggesting that ROS is formed from H_2O_2 decomposition.

To provide further evidence of superoxide production, NBT was used as a superoxide probe in solutions containing TEA, H_2O_2, and/or nC_{60}. Reaction of NBT with superoxide produces a purple-colored monoformazan moiety, which can be monitored via an increase in absorbance at 560 nm.[36] A solution composed of TEA+NBT exhibited a small increase in absorption likely due to photosensitized production of ROS by the NBT indicator itself (Fig. 5). Addition of nC_{60} to TEA+NBT did not elicit any significant change in superoxide production (Fig.S3). Conversely, addition of H_2O_2 to TEA+NBT resulted in increased $O_2^{\bullet -}$ production as indicated by an increase in absorbance at 560 nm. A further increase in $O_2^{\bullet -}$ production was observed when nC_{60} was added to TEA+NBT+H_2O_2, suggesting that nC_{60} catalyzes $O_2^{\bullet -}$ production from H_2O_2. Note that in a control experiment with nC_{60}+NBT+H_2O_2, no significant $O_2^{\bullet -}$ production was observed (Fig. S3). Consistently, when SOD (30 u/µL) was added as a superoxide quencher ($k(\text{SOD} + O_2^{\bullet -})=1.79 \times 10^9\ M^{-1}s^{-1}$),[35] IC degradation rate decreased for both light and dark conditions (Fig. 6). This result suggests that $O_2^{\bullet -}$ may be the major cause for IC degradation, while another form of ROS can be also responsible since the IC degradation rates were not completely quenched upon addition of excess SOD (Fig. S4).

To investigate the role of nC_{60} in ${}^{\bullet}OH$ production from H_2O_2, photochemical experiments were conducted using TA as a ${}^{\bullet}OH$ probe. Reaction solutions with only TA and H_2O_2 exhibited ${}^{\bullet}OH$ production as evidenced by an increase in fluorescence emission with increasing time. Upon addition of nC_{60}, the emission is partly quenched in a dose-dependent manner, suggesting that nC_{60} quenches ${}^{\bullet}OH$ production. nC_{60} has been shown to react with ${}^{\bullet}OH$ in water at diffusion-limited rates and may consume any ${}^{\bullet}OH$ species created in the IC/H_2O_2 system.[21] Consequently, ${}^{\bullet}OH$ consumption may partly contribute to the dominance of $HO_2^{\bullet}/O_2^{\bullet -}$ in the aqueous phase and may explain the observed pH dependence of IC degradation.

3.4. Postulated mechanism

The results presented herein suggest that nC_{60} plays an integral role in enhancing the degradation of IC in the presence of H_2O_2; nC_{60} seems to act as a catalyst for H_2O_2 decomposition to $HO_2^{\bullet}/O_2^{\bullet -}$ in the presence of an electron donor. We postulate that fullerene acts as an electron mediator, accepting an electron from excited IC and transferring it to an electron acceptor, such as H_2O_2 or perhydroxy radical (H_2O_2/H_2O E^0= +1.776 V; $HO_2^{\bullet}/H_2O_2$ E^0= +1.495 V vs NHE),[31, 37] thereby leading to oxidative degradation of IC. Note that $O_2^{\bullet -}$ does not likely act as an electron acceptor because of its large negative reduction potential ($O_2^{\bullet -}/O_2^{2\bullet -}$ E^0=–2.05 V vs SCE).[38] In fact, this agrees with the observed IC degradation rates as a function of pH, which was quite low above pH 5, where $O_2^{\bullet -}$ is the dominant form of $HO_2^{\bullet}/O_2^{\bullet -}$ acid-base pair. In the case of H_2O_2 as an electron acceptor, addition of an electron may also result in a photo-fenton like process, where H_2O_2 dismutates into hydroxyl radical and hydroxide ion according to $H_2O_2 + e^- \leftrightarrow {}^{\bullet}OH + OH^-$[28]. Analysis of IC and C_{60}'s HOMO-LUMO energy levels shows that electron transfer from IC's HOMO (−4.5 eV) to C_{60}'s LUMO (−4.5 eV) is plausible, but might proceed slowly because the levels are of the same energy.[39, 40] This electron transfer process may be enhanced by populating the excited states of IC and C_{60} because excited states possess better redox properties than ground states. As discussed above, excited C_{60} is a better oxidant than ground state C_{60} as evidenced by the reduction potentials of +1.1 V and −0.2 V vs. NHE for $^3C_{60}^*$ and C_{60}, respectively.[3] In fact, this claim agrees with observed IC degradation rates, which were enhanced upon UVA irradiation compared to a dark condition. Although the data presented herein strongly suggest that nC_{60} acts as an electron mediator under this specific condition, further experiments, for example, transient absorption spectroscopy to monitor $C_{60}^{\bullet-}$with femtosecond reolution[18], might be helpful to confirm this postulated electron transfer process.

4. Conclusions

Results from this study suggest that nC_{60} can play a key role in IC degradation and H_2O_2 decomposition by acting as an electron mediator in the presence of an electron donor under both light and dark conditions. This is one of the first reports to demonstrate that nC_{60} retains some of the redox properties of pristine C_{60} when dispersed in the aqueous phase. Although significant nC_{60} reduction was only found to occur at pHs below those typically encountered in the environment, nC_{60} may be redox active in select environmental scenarios such as in acidic soil media. Further studies on the reduction of nC_{60} using environmentally relevant electron donors and acceptors will provide more insight into the redox capabilities of nC_{60} in the natural environment.

Acknowledgements

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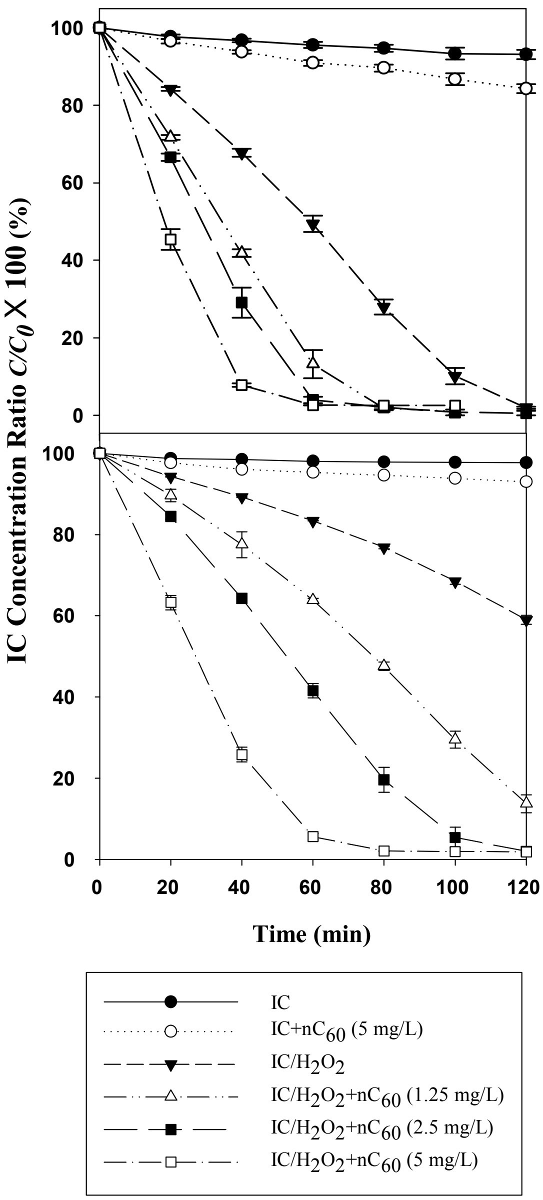

Fig. 1 IC degradation (C/C_o) as a function of time in the presence of H_2O_2 and nC_{60} at pH 3 under UV irradiation and (b) in the dark.

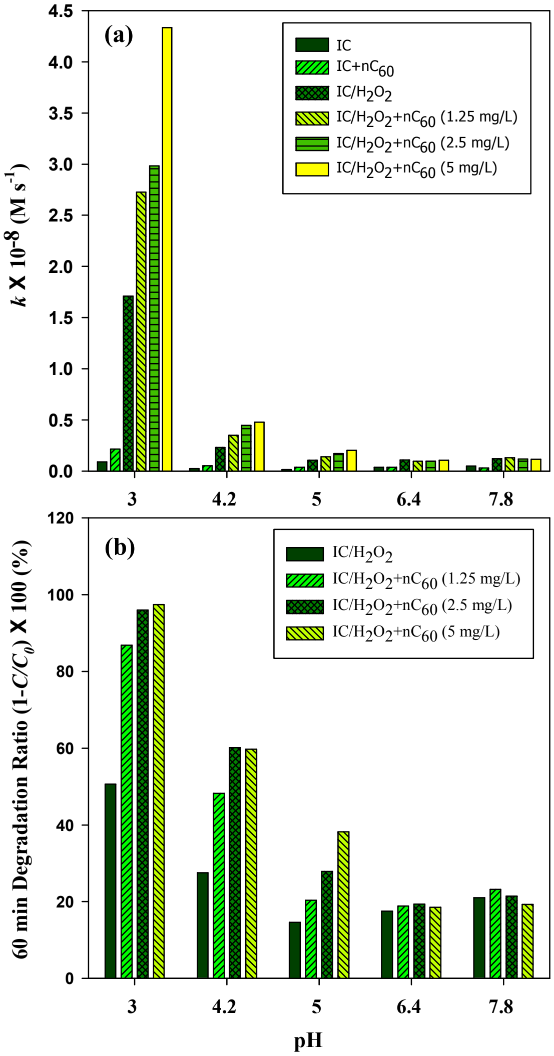

Fig. 2 Effect of pH on the degradation of IC under UV irradiation. (a) Zero-order reaction rate constants and (b) IC degradation ratio (*C/C$_o$*) after 60 min irradiation.

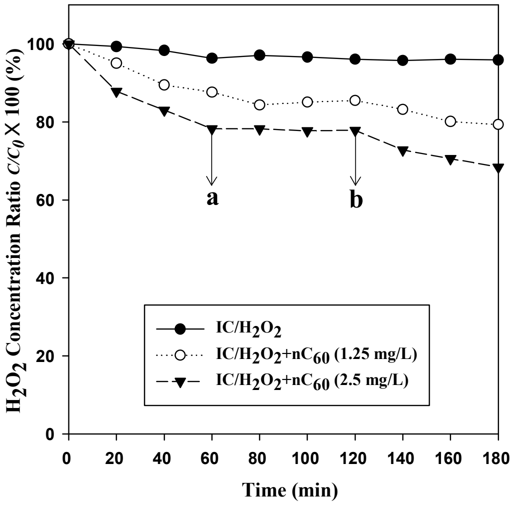

Fig. 3 Decomposition of H_2O_2 (C/C_o) as a function of time during IC degradation under UV irradiation at pH 3.

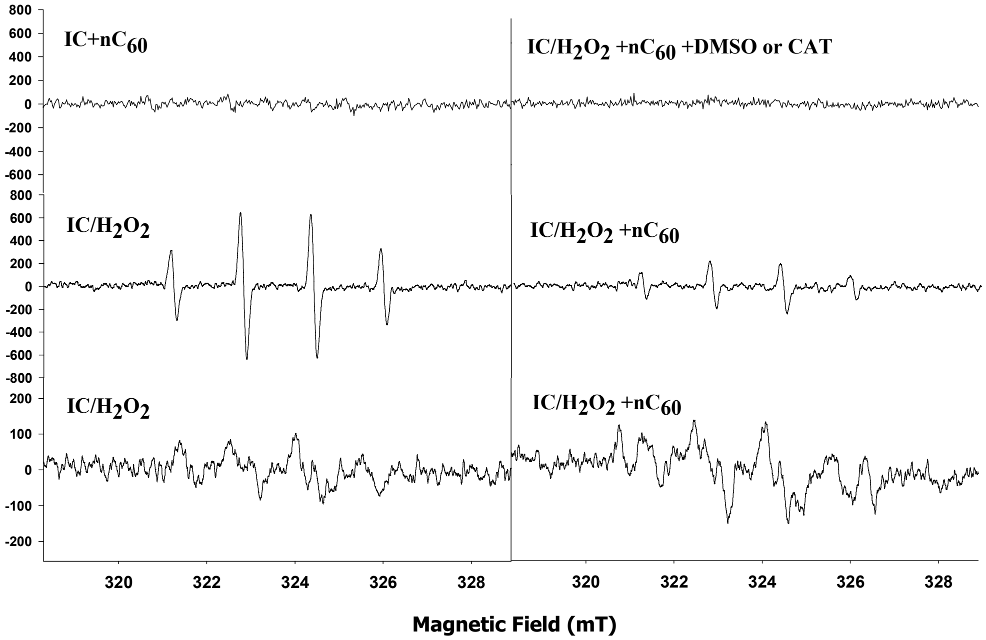

Fig. 4 EPR spectra of DMPO-OH· and DMPO-OOH· spin adducts produced in the solutions of various combinations of IC, H_2O_2, nC_{60} under UV illumination for 20 min. ($[DMSO]_0$=3.5 mM, $[CAT]_0$=0.3 u/μL).

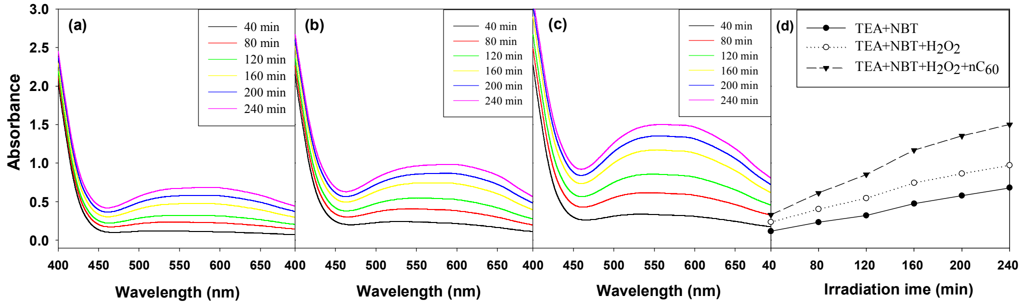

Fig. 5 UV-vis absorption spectra of removed reactor aliquots as a function of time under UV illumination for various solutions. (a) TEA+NBT, (b) TEA+NBT+H_2O_2, (c) TEA+NBT+H_2O_2+nC$_{60}$, (d) Absorbance intensity at 560 nm for (a)-(c).

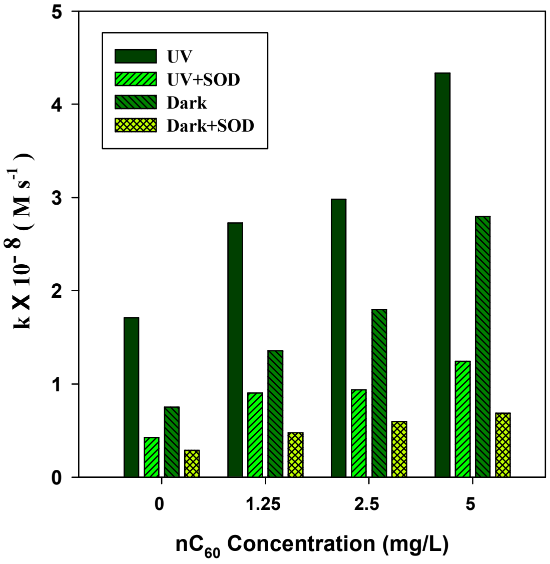

Fig. 6 Effect of SOD on zero-order reaction rate constant for IC degradation in the presence of H_2O_2 and nC_{60} in the dark and under UV irradiation. $[SOD]_0$=30 u/µL.

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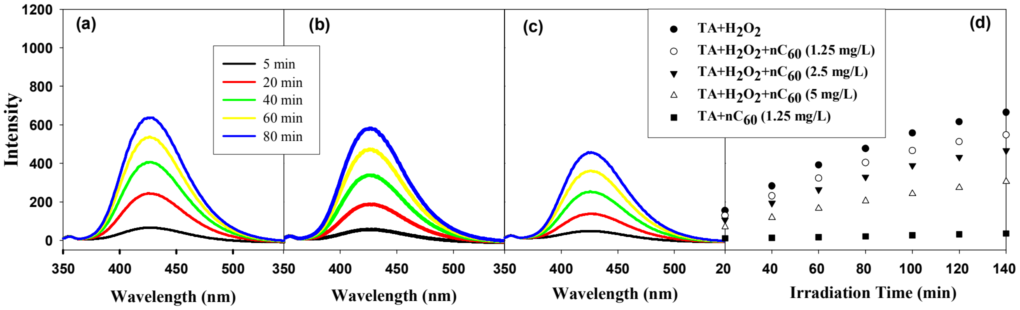

Fig.7 Fluorescence emission spectra of TA-OH adduct as a function of time for various combinations of reactor solutions irradiated with UV light. (a)TA+H_2O_2, (b) TA+H_2O_2+nC_{60} ([nC_{60}]$_0$=1.25 mg/L), (c)TA+H_2O_2+nC_{60} ([nC_{60}]$_0$=2.5 mg/L), (d) fluorescence emission intensity at 425 nm.