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Continuously photocatalytic production of H_2O_2 with high concentrations using 2-ethylanthraquinone as photocatalyst

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ABSTRACT

We report a photocatalytic process for H_2O_2 synthesis by using 2-ethylanthraquinone (EAQ) as photocatalyst. H_2EAQ (or HEAQ•) was in-situ produced by photocatalytic hydrogenation of EAQ with various solvents as hydrogen-donors (H-donors), and thus the pre-production of power-intensive H_2 was circumvented. The industrial hydrogenation of EAQ and the oxidation of H_2EAQ with O_2 here were combined into one pot for H_2O_2 photocatalytic production. EAQ molecule can be repeatedly used with high TON under both UV and visible light irradiation. When dual-phase reaction was adopted, the maximal H_2O_2 concentration of 574.0 mM in aqueous phase was achieved with mesitylene as H-donor. As the produced H_2O_2 concentration in the industrial AO process is estimated as ca. 400 mM in one cycle, our method with the dual-phase reaction greatly promotes the possibility for the practical production of H_2O_2 with photocatalytic method.

1. Introduction

As a green oxidant, hydrogen peroxide (H_2O_2) is widely used in industrial areas. More than 95% of the world's production of H_2O_2 so far is based on the anthraquinone oxidation (AO) process [1]. The main advantage of the AO process is the very high yield of H_2O_2 per cycle compared to other methods [2]. However, the input of large quantities of H_2 is indispensable, and risk of explosion exists if a certain amount of O_2 is mixed into the reactor. Recently, novel strategies for the production of H_2O_2 by other routes (electrochemical synthesis [3,4], direct synthesis [5,6], and so on) are being explored. Alternatively, photocatalytic production of H_2O_2 over semiconductor materials has been achieved, which is expected to reduce the production cost of H_2O_2 by using solar energy. Unfortunately, the concentrations of H_2O_2 produced with semiconductor heterogeneous photocatalytic methods (Table S1) are unimpressive, mM levels with UV irradiation [7–10] and μM levels with visible light irradiation [11–16] in most cases. To date, the highest concentrations of H_2O_2 produced through photocatalytic method just reach 40.2 mM under UV irradiation and 4.3 mM under visible irradiation, respectively [10].

Although new methods for H_2O_2 production are emerging in endlessly, AO process is still presented as the most competitive method for the industrial production of H_2O_2. Herein we report a photocatalytic method for the synthesis of H_2O_2 with 2-ethylanthraquinone (EAQ), in which EAQ is utilized as a homogeneous photocatalyst. H_2O_2 is photocatalytically produced with an hydrogen transfer process from the H-donor to the dissolved oxygen molecule via the assistance of the excited EAQ.

In industrial AO process, the production of H_2O_2 includes (i) the catalytic hydrogenation of EAQ with H_2 to 2-ethylanthrahydroquinone (H_2EAQ) and (ii) the oxidation of H_2EAQ with O_2 to give H_2O_2 and EAQ. The hydrogenation of EAQ is separated strictly from the oxidation of H_2EAQ [1]; otherwise, the reaction of O_2 with H_2 would trigger an explosion. Briefly, the solution containing H_2EAQ is separated from the hydrogenation catalyst (Nickel or supported Pd catalysts) and then oxidized with air to produce equimolecular amount of H_2O_2 and regenerate original EAQ as well [17]. In this work, the hydrogenation of EAQ adopted a photocatalytic method. The observation of photocatalytic hydrogenation process was firstly operated under N_2 atmosphere in the pre-deaerated solvent (CH_3CH_2OH) for safety consideration, although no additional H_2 was introduced into this system. H_2O_2 was then obtained by bubbling air for ca. 5 min after sampling.

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2. Experimental

2.1. Determination of H_2O_2

The concentration of H_2O_2 was determined by iodometric method with sodium thiosulfate ($Na_2S_2O_3$). Sample solution (1.0 mL) was added into iodine flask, and then H_2SO_4 (0.5 mL, 0.5 M) and KI solutions (0.5 mL, 100.0 g L^{-1}) were added. Two to three drops of 3% ammonium molybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) was added as catalyst to catalyze the generation of I_2. The solution was diluted with H_2O (several milliliters). After reaction of 10 min in the dark, the generated I_2 was titrated with $Na_2S_2O_3$. When the color turned yellowish, starch solution (1.0 mL, 10.0 g L^{-1}) was added for coloration, and then the titration went on until the blue disappeared and no longer appeared within 1 min.

In order to verify the accuracy of the iodometric method, the redox titration with $KMnO_4$ (calibrated with $Na_2C_2O_4$) was also used to determine the concentration of H_2O_2. The measurement error of the two methods is within 4%. Particularly, the measured H_2O_2 concentrations with the $KMnO_4$ redox titration were slightly larger than those with the iodometric method, which should be due to the additional $KMnO_4$ consumption from the organic contaminants.

2.2. Photocatalytic synthesis of H_2O_2

The photocatalytic synthesis of H_2O_2 was carried out in either mono-phase or dual-phase system. Mono-phase photocatalytic reaction was performed in ethanol solution, while dual-phase photocatalytic reaction was performed with organic phase to dissolve EAQ and aqueous phase to extract the generated H_2O_2.

2.2.1. Mono-phase photocatalytic reaction

2-Ethyl-9,10-anthraquinone (0.20 g, Sinopharm Chemical Reagent, 98%) was dissolved in ethanol (100 mL, Sinopharm Chemicals, >99.5%), and ultrasonicated 1 min for homogeneous dispersion. The reactions were operated under (i) deaerated condition with N_2 protection; (ii) atmosphere with simply sealed; and (iii) aerating condition with an air flow of 0.1 L min^{-1}, respectively. Particularly, the ethanol solvent was deaerated by ultrasonicating and vacuuming for 30 min in advance in the case of deaerated condition. The solution was then photoirradiated under magnetic stirring. At a regular interval, a volume of 3–4 mL was sampled, and then oxidated by air to obtain H_2O_2 from H_2EAQ.

2.2.2. Dual-phase photocatalytic reaction

2-Ethyl-9,10-anthraquinone (0.50 g) was dissolved in different solvents (80 mL). Double-distilled water (20 mL) was then added into the solution. The reactions were operated under aerating condition with an air flow of 0.1 L min^{-1}. The suspension was then photoirradiated under magnetic stirring. In the first several hours, 1.0 mL of sample in aqueous phase was taken out for the determination of H_2O_2 and equal amount of H_2O was added into the reaction liquid to make sure the volume of aqueous phase was not changed after sampling. When the concentration of H_2O_2 reached ca. 500 mM, more than 1.0 mL of sample was taken out in every 0.5 h to keep balance of the H_2O_2 concentration and stabilize it around 500 mM.

2.3. The method for HPLC and LC–MS analysis

HPLC (LC-20A, Shimadzu) and LC–MS (LCMS-IT-TOF, Shimadzu) were used to analyze EAQ and its oxidative intermediates. For the LC part, Inert Sustain C18 column (4.6 × 250 mm, 5 μm) was selected as the chromatographic column. Mobile phase condition: A/B = H_2O/CH_3OH; 0–1 min, 60% B; 1–10 min, gradient change from 60% B to 82% B; 10–18 min, 82% B; 18–30 min, 60% B; flow rate: 1.0 mL min^{-1}. DAD detector was used to trace the substances.

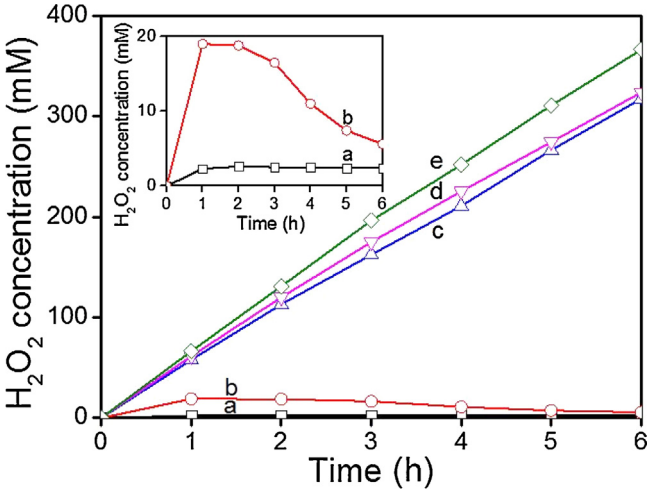


Fig. 1. The photocatalytic H_2O_2 production in ethanol with (a) deaerated condition, (b) simply sealed condition, and aerating with an air flow of (c) 0.05 L min^{-1}, (d) 0.1 L min^{-1}, (e) 0.2 L min^{-1}. Inset: zoomed curves of (a) and (b). The concentration of EAQ: 2.0 g L^{-1}.

For the MS part, atmospheric pressure chemical ionization (APCI) was selected as the ion source, and a high resolution TOF detector was used. Ion source interface voltage: 4.5 kV, −3.5 kV; Nebulizer gas: N_2, 1.5 L min^{-1}; Drying gas: N_2, 10 L min^{-1}; Oven temperature: 40 °C; Interface temperature: 300 °C; CDL temperature: 250 °C; Heating block temperature: 250 °C; Detector voltage: 1.6 kV.

2.4. The method for GC analysis

Quantitative analysis of toluene and its reaction products were performed using gas chromatograph (Agilent GC 7890B) with a capillary column (Agilent DB-17, 30 m × 0.25 mm × 0.5 μm) and a FID detector. *o*-Dichlorobenzene was used as internal standard substance for the quantitative analysis of benzaldehyde. Injector temperature: 250 °C; Detector temperature: 300 °C. Oven temperature was programmed as follows: the initial temperature was set at 50 °C, followed by constant heating rate of 10 °C min^{-1} until the final temperature of 280 °C was attained and held for 5 min. The carrier gas was N_2 with the flow of 1 mL min^{-1}, and the splitting ratio was set as 20:1.

3. Results and discussion

3.1. Mono-phase photocatalytic reaction

A considerable amount of H_2O_2 was produced just with the help of EAQ in the homogeneous system of ethanol (Fig. 1). The concentration of H_2O_2 got the maximal value (2.6 mM) in 2.0 h, and then kept almost unchanged, i.e., the relative content of H_2EAQ to EAQ kept a chemical equilibrium. In other word, the hydrogenation of the EAQ here is limited a lot for the dynamic restriction. Specifically, the extent of hydrogenation (conversion of EAQ to H_2EAQ) only reaches ca. 30% in this situation, which is far below that adopted in industrial AO process (up to 60–70%) [1,18,19]. The hydrogenation of EAQ in this system is achieved with a mild EAQ photocatalytic process, in which H_2 is substituted by the H-containing solvent (CH_3CH_2OH), and the delusional danger from the violent reaction between H_2 and O_2 is actually inexistent. Therefore, the photocatalytic hydrogenation of EAQ seems available in the presence of O_2, which suggests one-pot production of H_2O_2 can be possibly

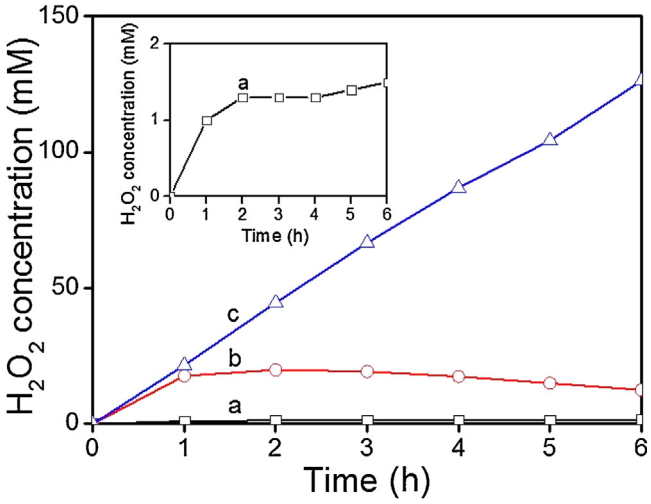


Fig. 2. The photocatalytic H_2O_2 production under visible irradiation (λ > 420 nm) in ethanol with (a) deaerated condition, (b) simply sealed condition, and (c) aerating with an air flow of 0.1 L min^{-1}. Inset: zoomed curve of (a). The concentration of EAQ: 2.0 g L^{-1}.

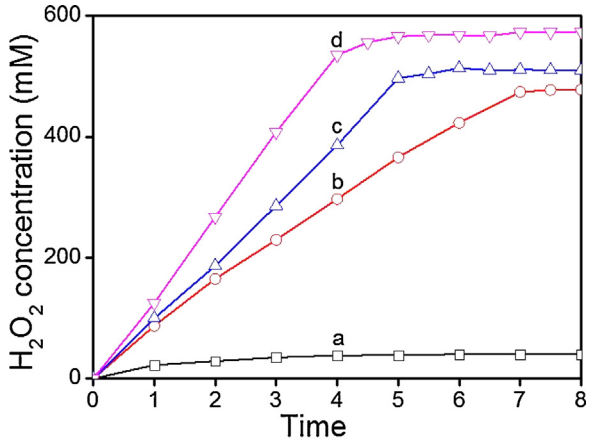


Fig. 3. Dual-phase photocatalytic production of H_2O_2 in aerating condition (0.1 L min^{-1}) with (a) ethyl acetate, (b) toluene, (c) xylene, and (d) mesitylene as H-donors. Organic phase: 80 mL; H_2O: 20 mL. EAQ: 0.5 g.

achieved. Besides, the produced concentration of H_2O_2 in a single cycle is severely limited by the EAQ concentration used in the traditional AO route. However, as EAQ can be circularly used in the homogeneous photocatalytic process here, the concentration limitation for producing H_2O_2 can possibly be solved. Therefore, the photocatalytic reactions were also carried out in a simply sealed flask (un-deaerated & un-aerating) as well as under an aerating condition.

It should be noted that as the concentration of EAQ in ethanol is limited to 8.46 mM according to its solubility, the maximal concentration of H_2O_2 could achieve 8.46 mM at most if the generation of H_2EAQ was one-off. However, as shown in Fig. 1, the concentration of H_2O_2 reached the maximal value of 19.0 mM at 1.0 h for the simply sealed case, i.e., the produced H_2O_2 concentration limitation from the EAQ solubility is broken. It is suggested that the EAQ molecules here repeatedly reacted to trap the H-atom from the H-donor and then liberate the H-atom to the oxygen molecules. However, when the dissolved oxygen molecules were exhausted, the as-formed H_2O_2 would be further hydrogenated to H_2O by interacting with the hydrogen-trapped EAQ. Therefore, although the direct hydrogenation of H_2O_2 to H_2O has a relatively high activation barrier [20], the concentration decrease of H_2O_2 becomes

Table 1
The production capacity of the crude H_2O_2 aqueous solution with various H-donors in aerating condition under full-spectrum irradiation.

System	Solvent	K^a (mM h^{-1})	$C_a{}^b$ (mM)	V^c (mL h^{-1})	$C_o{}^d$ (mM)
Mono-phase	ethanol	54.0/21.0	/	/	/
Dual-phase	ethyl acetate	22.5/8.3	40.3	1.0	10.6
	toluene	74.3/17.7	478.0	3.0	32.5
	xylene	99.4/24.4	500.0	4.0	54.5
	mesitylene	133.8/33.7	574.0	5.0	64.5

[a] The reaction rate constant under full-spectrum/visible irradiation.
[b] The final concentration of H_2O_2 in aqueous phase.
[c] The output of crude H_2O_2 aqueous solution every one hour at equilibrium stage.
[d] The final concentration of H_2O_2 in organic phase.

unavoidable (Fig. 1). Similar problem has also emerged in the direct synthesis of H_2O_2 with H_2 and O_2, in which the sequential hydrogenation of H_2O_2 to H_2O possibly occurs after the generation of H_2O_2 [21,22].

As for the aerating case (blowing air with a gas flow of 0.05 L min^{-1}), the production of H_2O_2 was well maintained with a steady formation rate of ca. 53 mM h^{-1} and gave a final concentration of 317.5 mM in 6.0 h. When increasing the air flows to 0.1 and 0.2 L min^{-1}, the concentration of H_2O_2 increased some to 324.0 and 366.5 mM (i.e., 12.5 g L^{-1}). Surely, the supply of O_2 indeed had a great impact on the H_2O_2 production. In the presence of O_2, the hydrogen-transfer channal from the hydrogen-trapped EAQ undergoes smoothly. The produced concentration of H_2O_2 in 6.0 h (with a gas flow of 0.2 L min^{-1}) is calculated to be 43.3-fold as the concentration of EAQ used here. Besides, the over-hydrogenation of H_2O_2 is not observed with air blowing. The process to produce H_2O_2 in the presence of O_2 is a little different from that in deaerated condition. When in deaerated condition, excited EAQ captures H-atoms from the H-donor (here refers to ethanol) to form H_2EAQ under irradiation. Then the H_2EAQ is oxidized with O_2 (when air blowing at the second step) to produce H_2O_2 and original EAQ, which is similar to the industrial AO process. However, in the present of O_2, when the excited EAQ molecule abstracts one H-atom from the H-donor to form a protonated semiquinone radical [23], a rapid reaction between the semiquinone radical and O_2 would occur, in which the semiquinone radical transports H to O_2 to form the hydroperoxyl radical ($HO_2^{\bullet}$) [24–29], which subsequently dismutates to form H_2O_2 as shown in Eqs. (1)–(3). Therefore, the repeated use of EAQ can be achieved for the H_2O_2 production, which greatly breaks through the concentration limit of EAQ.

$$EAQ \xrightarrow{h\nu} EAQ* \xrightarrow{\text{H-donor}} HEAQ^{\bullet} + D^{\bullet} \quad (1)$$

$$HEAQ^{\bullet} + O_2 \rightarrow EAQ + HO_2^{\bullet} \quad (2)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (3)$$

According to the significant visible light absorbance of EAQ (Fig. S1 and Table S2), the visible light activity of EAQ was also tested by cutting off the UV band with an optical filter (λ > 420 nm). The similar tendencies of H_2O_2 production were observed as shown in Fig. 2. In the case of pre-deaerated reaction, the concentration of H_2O_2 increased slowly and reached the maximal value of 1.5 mM in 6.0 h. In the condition of limited O_2-supply (simply sealed), the produced maximal concentration of H_2O_2 was enhanced to 19.9 mM in 2.0 h with a much faster rate. However, after the exhaustion of O_2, the production of H_2O_2 was blocked and the H_2O_2 concentration turned to decrease with a slower rate compared to that with the full-spectrum irradiation. Air-blowing gave a stable O_2-supply and enhanced the total amount of H_2O_2 production. The concentration of H_2O_2 was stepwise accumulated to 126.2 mM after irradiation for 6.0 h, which is about 39% of the produced H_2O_2 concentration obtained with full-spectrum irradiation in the same condition. In brief, the photocatalytic production of H_2O_2 with EAQ exhibits

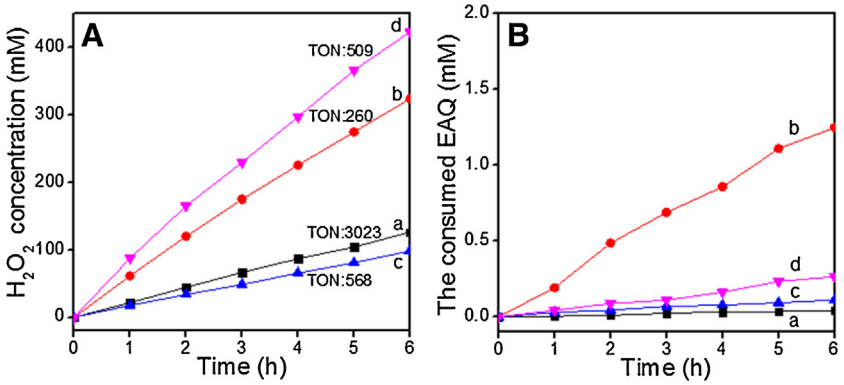
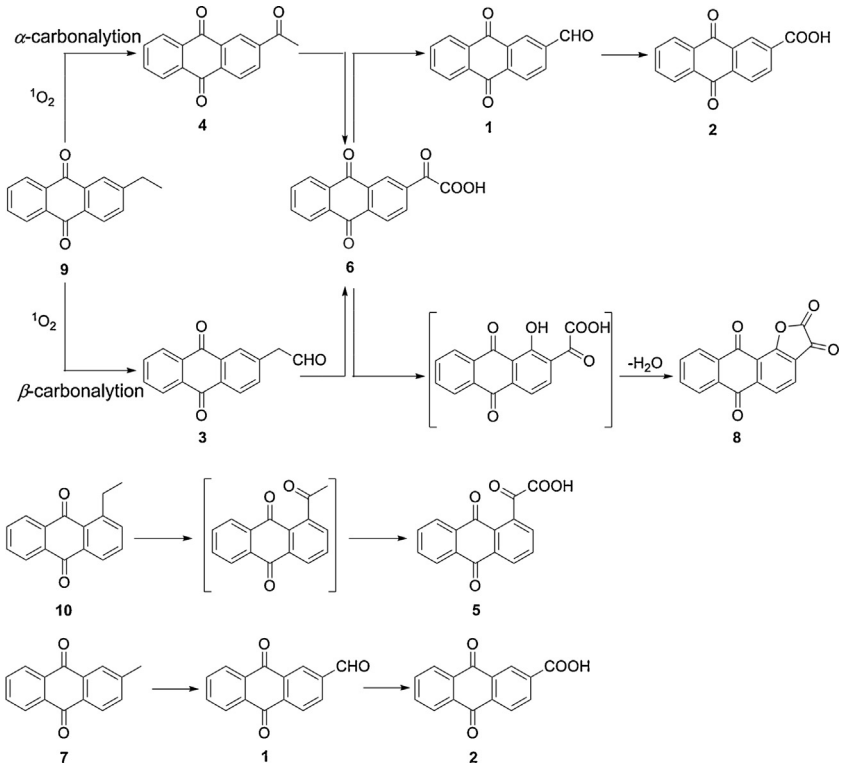


Fig. 4. Production of H_2O_2 (A) and consumption of EAQ (B) vs irradiation time in aerating condition (0.1 L min^{-1}). The samples were taken from the reactions operated in ethanol under (a) visible irradiation & (b) full-spectrum irradiation, and in toluene under (c) visible irradiation & (d) full-spectrum irradiation.



Scheme 1. The evolution of EAQ and impurities in the photocatalytic production of H_2O_2.

extremely high efficiencies under both UV and visible irradiation, although mere visible irradiation is relatively weaker in exciting EAQ (with the maximum absorption peak in 256 nm, see Fig. S1) for H_2O_2 production.

3.2. Dual-phase photocatalytic reaction

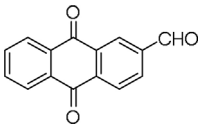
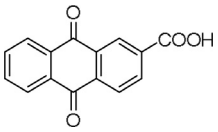
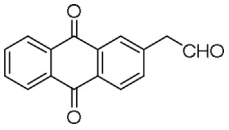
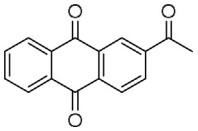
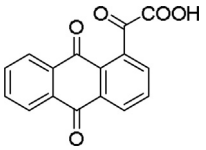
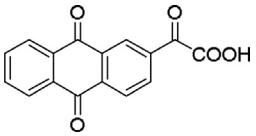
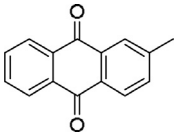
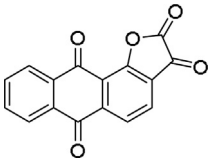
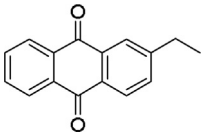
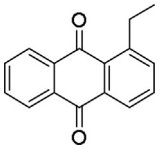
In order to directly obtain a crude H_2O_2 aqueous solution of high concentration to simulate the practical H_2O_2 production, the dual-phase photocatalytic reaction with organic phase to dissolve EAQ and aqueous phase to extract the generated H_2O_2 was operated (Fig. 3). Different methyl benzenes and ethyl acetate were used as organic solvents to dissolve EAQ as well as supply hydrogen atoms. The produced concentration of H_2O_2 in aqueous phase was monitored every 1.0 h until the concentration of H_2O_2 reached ca. 500 mM. Then a certain amount of H_2O_2 aqueous solution (more than 1.0 mL) was taken out and an equal amount of water was added back in for every 0.5 h. In this way, a crude H_2O_2 aqueous solution of ca. 500 mM was obtained as shown in Fig. 3.

Ethyl acetate is a poor H-donor. The H_2O_2 production reached balance in 4 h and then the concentration of H_2O_2 kept at a low concentration (ca. 40 mM) with no increase. On the contrary, methyl benzenes exhibited excellent performances. The initial formation rates of H_2O_2 were estimated as 22.5, 74.3, 99.4 and 133.8 mM h^{-1} for ethyl acetate, toluene, xylene, and mesitylene, respectively. The output of the crude H_2O_2 aqueous solution with these H-donors (at the balance stage) were summarized and listed in Table 1 with other concerned parameters. The concentrations of H_2O_2 in organic phases were also determined and listed in Table 1.

3.3. The oxidative pathway of toluene

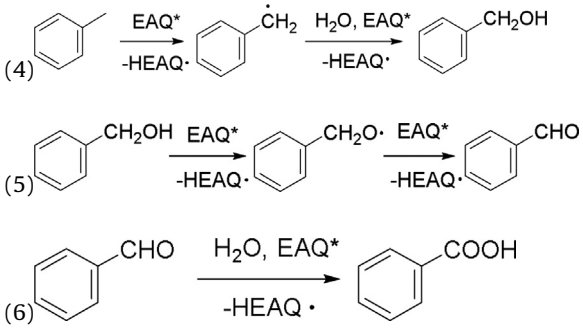
Toluene was selected as the model H-donor here to analyze the possible oxidative pathway of methyl benzenes by determining its products after reaction for 8.0 h. Benzaldehyde was determined to

Table 2
EAQ and its oxidative intermediates identified with LC–MS.

Entry	Time	Formula	*m*/*z*	Substance	Structure
1	7.793	$C_{15}H_8O_3$	236.0860	anthraquinone-2-carbaldehyde	
2	10.455	$C_{15}H_8O_4$	252.0779	anthraquinone-2-carboxylic acid	
3	10.925	$C_{16}H_{10}O_3$	250.0635	anthraquinone-2-acetaldehyde	
4	12.738	$C_{16}H_{10}O_3$	250.0636	2-acetyl-anthraquinone	
5	13.706	$C_{16}H_8O_5$	280.1115	anthraquinone-1-oxoacetic acid	
6	14.856	$C_{16}H_8O_5$	280.1099	anthraquinone-2-oxoacetic acid	
7	17.464	$C_{15}H_{10}O_2$	222.0703	2-methyl-anthraquinone	
8	17.729	$C_{16}H_6O_5$	278.0940	anthraquinone-1,2-furandione	
9	20.419	$C_{16}H_{12}O_2$	236.0811	EAQ	
10	22.275	$C_{16}H_{12}O_2$	236.0824	1-ethyl-anthraquinone	

be 7.37 mmol (i.e., 0.94% in mass fraction) in organic phase with GC. However, no benzyl alcohol was detected. Further, benzoic acid was measured to be 1.54 mmol in organic phase and 0.22 mmol in aqueous phase by HPLC, with its distribution ratio in toluene and water to be 6.9. These results suggested that the excited EAQ seized H from the toluene molecule to form a benzyl radical as seen in Eq. (4), and the benzyl radical further tansformed to benzyl alcohol in the presence of H_2O. As a better H-donor, benzyl alcohol was more preferential to lose its hydroxylic H by the excited EAQ, and transformed itself into benzaldehyde. Similar results (i.e., α-

carbonylation without significant α-hydroxylated intermediates) have been previously reported in the alkylbenzene oxidation in other photocatalytic reactions [30–32]. The further oxidation of benzaldehyde with the excited EAQ then led to the produce of benzoic acid.



3.4. The turnover number (TON) of EAQ and its oxidative intermediates

HPLC analysis was applied to track the concentration changes of EAQ during the reaction (Fig. 4B). It should be noted that, the concentration of EAQ remained almost unchanged under visible light irradiation although O_2 was bubbled through the solution. On the other hand, EAQ slowly decreased with time and dropped by ca. 1.24 mM in 6 h under full-spectrum irradiation in the presence of O_2. The decomposition of EAQ should be due to its oxidation by singlet oxygen [33]. It has been reported that an energy transfer between the excited EAQ molecule and oxygen molecule would occur under irradiation [34], which leads to the generation of singlet oxygen. Academically, only ca. 1.24 mM, i.e. 14.7% of EAQ, changed with a H_2O_2 production of 324.0 mM, which gave a TON of 260 in the lifetime of EAQ under full-spectrum irradiation. As for the case of visible irradiation, no apparent loss (0.04 mM, 0.5%) of EAQ was observed for H_2O_2 production of 126.2 mM with a TON of 3023. The reason for the apparent difference of TONs between these two cases may be due to that UV irradiation is more effective in producing $^1O_2$, which then reacts with EAQ, leading to the oxidation of EAQ. By changing the solution from ethanol to toluene, the TONs for the H_2O_2 production turn into to 509 under full-spectrum irradiation and 568 under visible irradiation, with an EAQ loss of 0.26 mM and 0.08 mM in toluene, respectively. The enhancement of the TON of EAQ in toluene solution under full-spectrum irradiation should be due to the weaker polarity of toluene compared to ethanol, which suppressed the formation of $^1O_2$ with stronger polarity. However, the low efficiency of H_2O_2 production led to only a little increase of TON when under visible irradiation.

Correspondingly, the oxidative intermediates of EAQ were analyzed by LC–MS (Figs. S2–S12). Table 2 listed the main substances in EAQ solution identified by LC–MS. Besides EAQ itself, there are 10 substances existing. Substances **7** and **10** are identified as 2-methyl-anthraquinone and 1-ethyl-anthraquinone (isomer of EAQ), respectively. Both of them appeared in the raw EAQ solution with low contents (both below 1.0%) and then disappeared after the photocatalytic reaction. Presumably, they may come from the industrial synthetic process of EAQ with phthalic anhydride and ethylbenzene through Friedel-Crafts reaction [35,36].

Scheme 1 depicted the possible oxidative pathways of EAQ. Unlike the case in industrial process, EAQ molecules here suffered from oxidation to form oxidized products, although these changes did not bring obvious harm to the practical efficiency of H_2O_2 production. During photocatalytic reaction, the ethyl in the excited EAQ was attacked by $^1O_2$ (O_2 excited by EAQ*) [34,37] and formed corresponding ketone (substance **4**, major) or aldehyde (substance **3**, minor). Further oxidation then led to the formation of anthraquinone-2-oxoacetic acid (substance **6**). Anthraquinone-2-oxoacetic acid was not quite stable and decomposed to form anthraquinone-2-carbaldehyde (substance **1**, minor) and anthraquinone-2-carboxylic acid (substance **2**, major), or further oxidized to form α-hydroxyl compound, which was then esterified intramolecularly to form cyclic lactone (substance **8**). On the other hand, the oxidation of 1-ethyl-anthraquinone (substance **10**) gave anthraquinone-1-oxoacetic acid (substance **5**), while the oxidation of 2-methyl-anthraquinone (substance **7**) gave anthraquinone-2-carbaldehyde (substance **1**) and anthraquinone-2-carboxylic acid (substance **2**) through similar processes. All these substances got changed only in their side chains and the structure of 9,10-anthraquinone remained unchanged; therefore, little influence can be observed on the efficiency of H_2O_2 production with the oxidation of EAQ, which conformed to results shown in Figs. 1–3.

4. Conclusions

In summary, we provided a photocatalytic process for H_2O_2 synthesis with EAQ as photocatalyst and various solvents as H-donors. Compared to industrial AO process, the pre-production of power-intensive H_2 is circumvented by using light irradiation to in-situ produce H_2EAQ (or HEAQ•) in this work. Therefore, one pot reaction for the production of H_2O_2 is available by combining the industrial hydrogenation step of EAQ and the oxidation step of H_2EAQ (HEAQ•) with O_2 into one reactor. Further, as EAQ molecule can be repeatedly used with high TON for H_2O_2 production in this photocatalytic reaction, the dissolution of EAQ (and H_2EAQ) with great amount is not crucial anymore. Compared with other photocatalytic methods, our method significantly enhances the produced concentrations of H_2O_2 under both UV and visible light irradiation. Considering that the practical H_2O_2 concentration in industrial AO process is estimated as ca. 400 mM [19] before the final concentration treatment, our method with the dual-phase reaction gives a raw H_2O_2 concentration beyond 470 mM (max. 574.0 mM with mesitylene), which greatly promotes the possibility for the practical production of H_2O_2 with the photocatalytic method.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2016.04.009.

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