

Appendix 1: Coumarin and Fricke dosimeters

The rate of 7OH-C3CA production ($r(7\text{OH-C3CA}) = 1.6 \cdot 10^{-5} \mu\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$) was obtained as the slope of linear fit of the dependence of 7OH-C3CA concentration on irradiation time (Fig. A1). The efficiently absorbed energy measured by coumarin dosimeter was expressed as the energy absorbed in 1 kg per 1 second (i.e. “dose rate”, D) (eqn. A1) using known radiation chemical yield of 7OH-C3CA $G(7\text{OH-C3CA}) = 0.015 \mu\text{mol} \cdot \text{J}^{-1}$ and the density of the dosimetric solution $\rho(\text{coumarin}) = 1.0026 \text{ kg} \cdot \text{dm}^{-3}$.

$$D(\text{coumarin}) = \frac{r(7\text{OH-C3CA}) [\mu\text{l}]}{G(7\text{OH-C3CA}) [\mu\text{mol} \cdot \text{J}^{-1}] \cdot 1.1 \cdot 10^{-3} \text{ J} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}} \quad (\text{A1})$$

This value was used for the determination of the quantum yield of $\cdot\text{OH}$ radicals under 253.7-nm irradiation.

The rate of Fe^{3+} production ($r(\text{Fe}^{3+}) = 2.9 \cdot 10^{-2} \mu\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$) was obtained as the slope of linear fit of the dependence of Fe^{3+} concentration on irradiation time (Fig A1). Efficiently absorbed energy measured by Fricke dosimeter was expressed in the same way as by the coumarin dosimeter (eqn. A1) using known radiation chemical yield of Fe^{3+} ($G(\text{Fe}^{3+}) = 1.62 \mu\text{mol} \cdot \text{J}^{-1}$) and the density of Fricke solution ($\rho(\text{Fricke}) = 1.024 \text{ g} \cdot \text{cm}^{-3}$)³. We obtained value of $D(\text{Fricke}) = 1.7 \cdot 10^{-2} \text{ J} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$.

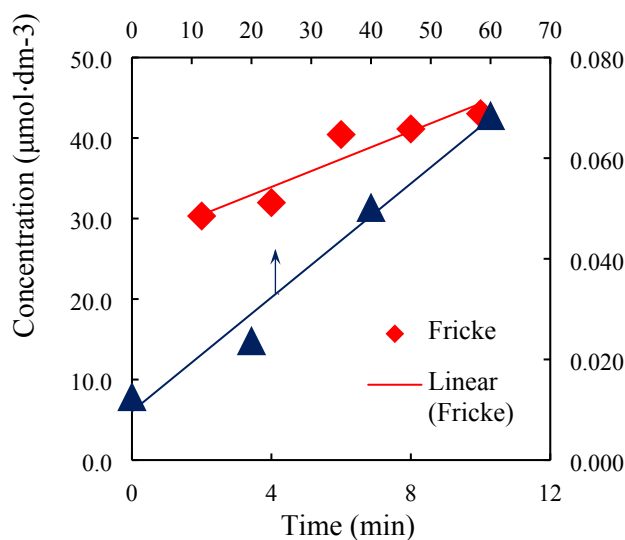


Figure A1: Concentration of 7OH-C3CA or Fe^{3+} formed under UV irradiation in coumarin and Fricke dosimeters, respectively.

Appendix 2: Radiation chemical yield of H₂O₂

In the system under study, we assume that H· and ·OH radicals are formed exclusively by the dissociation of excited triplet state of H₂O molecules. It follows that an H₂O₂ molecule may be formed only via recombination of two ·OH radicals (Fig. A2).

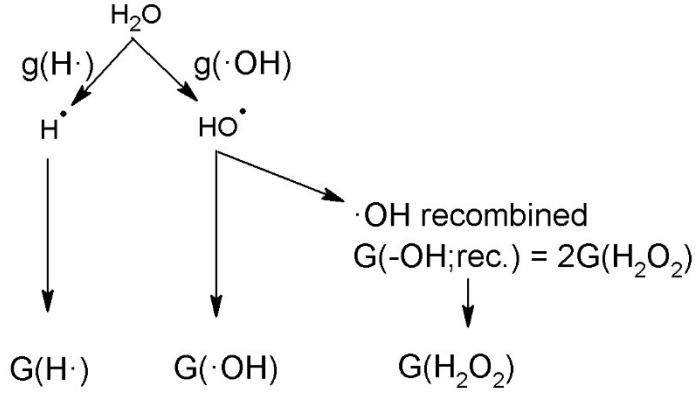


Figure A2: Products of 253.7-nm water photolysis, where g corresponds to primary radiation chemical yields and G to radiation chemical yields of products. $G(-OH;rec.)$ corresponds to ·OH radicals that recombined to form H₂O₂.

Following relations apply for radiation chemical yields:

$$G(Fe^{3+}) = G(\cdot OH) + 2G(H_2O_2) + G(H\cdot) \quad (A2)$$

$$G(H\cdot) = G(\cdot OH) + 2G(H_2O_2) \quad (A3)$$

To evaluate the part of ·OH radicals formed via dissociation of water triplet state and subsequently recombined, we considered the relations of competitive kinetics.



In the equations, k_{Fe} and $k_{\cdot OH}$ denote rate constants for reaction of ·OH radical with Fe²⁺ and recombination of two ·OH radicals, respectively. Following relations apply for the concentrations of reactants:

$$-\frac{d[Fe^{2+}]}{dt} = k_{Fe} \cdot [Fe^{2+}] \cdot [\cdot OH] \quad (A6)$$

$$-\frac{d[\cdot OH]}{dt} \Big|_{rec} = k_{\cdot OH} \cdot [\cdot OH] \cdot [\cdot OH] \quad (A7)$$

$$\left(-\frac{d[\cdot OH]}{dt}\right)_{tot} = -\frac{d[Fe^{2+}]}{dt} - \left(\frac{d[\cdot OH]}{dt}\right)_{rec} = k_{Fe} \cdot [Fe^{2+}] \cdot [\cdot OH] \quad (A8)$$

In the equations, $\left(-\frac{d[\cdot OH]}{dt}\right)_{rec}$ denotes the decrease of $\cdot OH$ radical concentration due to recombination, whereas $\left(-\frac{d[\cdot OH]}{dt}\right)_{tot}$ denotes the decrease of $\cdot OH$ radical concentration due to both recombination and reaction with Fe^{2+} . We may now express the probabilities P for reactions of $\cdot OH$ radicals with Fe^{2+} and recombination processes:

$$P(Fe^{2+} + \cdot OH) = \frac{k_{Fe} \cdot [Fe^{2+}] \cdot [\cdot OH]}{k_{Fe} \cdot [Fe^{2+}] \cdot [\cdot OH] + k_{\cdot OH} \cdot [\cdot OH] \cdot [\cdot OH]} \quad (A9)$$

$$P(\cdot OH + \cdot OH) = \frac{k_{\cdot OH} \cdot [\cdot OH] \cdot [\cdot OH]}{k_{Fe} \cdot [Fe^{2+}] \cdot [\cdot OH] + k_{\cdot OH} \cdot [\cdot OH] \cdot [\cdot OH]} = \quad (A10)$$

To calculate the probabilities, the concentration $[\cdot OH]$ needs to be quantified. The determined production rate of 7OH-C3CA $r(7OH-C3CA) = 1.6 \cdot 10^{-5} \mu mol \cdot dm^{-3} \cdot s^{-1}$ can be recalculated as $\cdot OH$ radical production rate $r(\cdot OH)$:

$$r(\cdot OH) = \frac{r(7OH-C3CA)[mol \cdot d]}{0.06} = 0.72 = 1.9 \cdot 10^{-10} mol \cdot d \quad (A11)$$

where 0.06 is the factor obtained in literature, taking into account that only 6 % of $\cdot OH$ radicals participate on formation of fluorescent 7OH-C3CA. The ratio $\frac{G(\cdot OH)_{\gamma, lit}}{G(\cdot OH)_{\gamma, determined}} = 0.72$ is the correction factor determined via gamma irradiation of C3CA (see 3.2. in the article for details).

With the known concentration of Fe^{2+} in Fricke dosimeter ($0.001 mol \cdot dm^{-3}$), known production rate of $\cdot OH$ radicals ($1.9 \cdot 10^{-10} mol \cdot dm^{-3} \cdot s^{-1}$) and the rate constants as $k_{Fe} = 4.3 \cdot 10^8 dm^3 \cdot mol^{-1} \cdot s^{-1}$ and $k_{\cdot OH} = 5.5 \cdot 10^9 dm^3 \cdot mol^{-1} \cdot s^{-1}$, we obtained the probability (in time = 1 s) of the reaction with Fe^{2+} $P(Fe^{2+} + \cdot OH) = 0.999998$. The probability of the recombination equals to $P(\cdot OH + \cdot OH) = 2.5 \cdot 10^{-6}$, which is negligible.

It follows that we can use simplified equation 12 in the main paper.

Appendix 3: The dependence of quantum yield of $\cdot\text{OH}$ radicals on wavelength

The dependence of quantum yield of $\cdot\text{OH}$ radicals on wavelength of UV radiation⁵ in Table 1 in the article, including our result of quantum yield of $\cdot\text{OH}$ radicals under 253.7-nm irradiation, follows an exponential trend as shown in Figure A3.

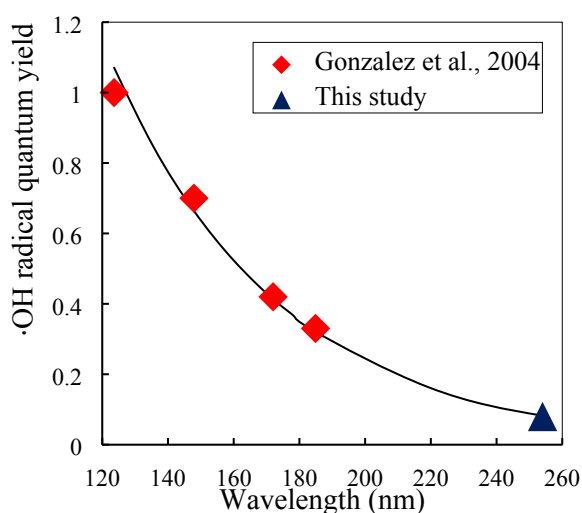


Figure A3: The dependence of quantum yield of $\cdot\text{OH}$ radicals $\Phi(\cdot\text{OH})$ on wavelength λ of UV radiation.

References:

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