Supporting Information

High Sample Throughput LED Reactor for Facile Characterization of the Quantum Yield Spectrum of Photochemically Produced Reactive Intermediates

Binbin Wu[†], Tian Liu[†], Yanling Wang[†], Guoqiang Zhao[†], Baoliang Chen[†], and Chiheng Chu[*†]

[†]Department of Environmental Science, Zhejiang University, Hangzhou 310058, China
[*]Corresponding Author: chuchiheng@zju.edu.cn

Section S1. Chemical sources and preparations

All reagents were used as received without further purification. Suwannee River Natural Organic Matters (SRNOM) were purchased from the International Humic Substances Society (IHSS). Resorufin and horseradish peroxidase (HRP) were obtained from Sigma Aldrich. 2,4,6-trimethylphenol (TMP), Furfuryl alcohol (FFA), potassium terephthalic acid (TPA), and hydroxyterephthalic acid (hTPA) were purchase from Shanghai Aladdin Chemical Reagent Company. Ampliflu Red was obtained from Shanghai Macklin Biochemical Co., Ltd. TMP was used as a probe to determine the steady-state $^3CDOM^*$ concentrations in the bulk aqueous phase ($[^3CDOM^*]_{ss}$).[1] FFA was used to probe $[^1O_2]_{ss}$.[2] Ampliflu Red reacted with H_2O_2 in the presence of HRP and formed the fluorescent product resorufin.[3] TPA reacted with $^{\bullet}OH$ via hydroxylation and form the fluorescent product hTPA and was used as a probe to determine the cumulative $^{\bullet}OH$ formation.[4]

Section S2. LED light photoreactor device.

Eight monochromatic LED bulbs and 1 broadband LED bulb (simulated sunlight) were assembled in a custom-made light plate (**Figure S1a**) and placed on a commercial photoreactor (**Figure S1b**, model slight; Perfect Light, Inc.). Quartz vials were applied for all photolyses. Under working conditions, the solutions were irradiated from the bottom of the quartz vial. Each light was separated by a thick reactor wall (**Figure S1b** and **S1c**). Therefore, the photoreaction will not be affected by the irradiance from neighboring lights. The device working current was adjusted through altering the resistance of the potentiometer. We note that the photon flux of LED lights were different at the same working current (**Figure S1d**). To assess the PPRIs quantum yield, we applied a working current of 38%, where the irradiance of simulated sunlight was 100 mW/cm^2.

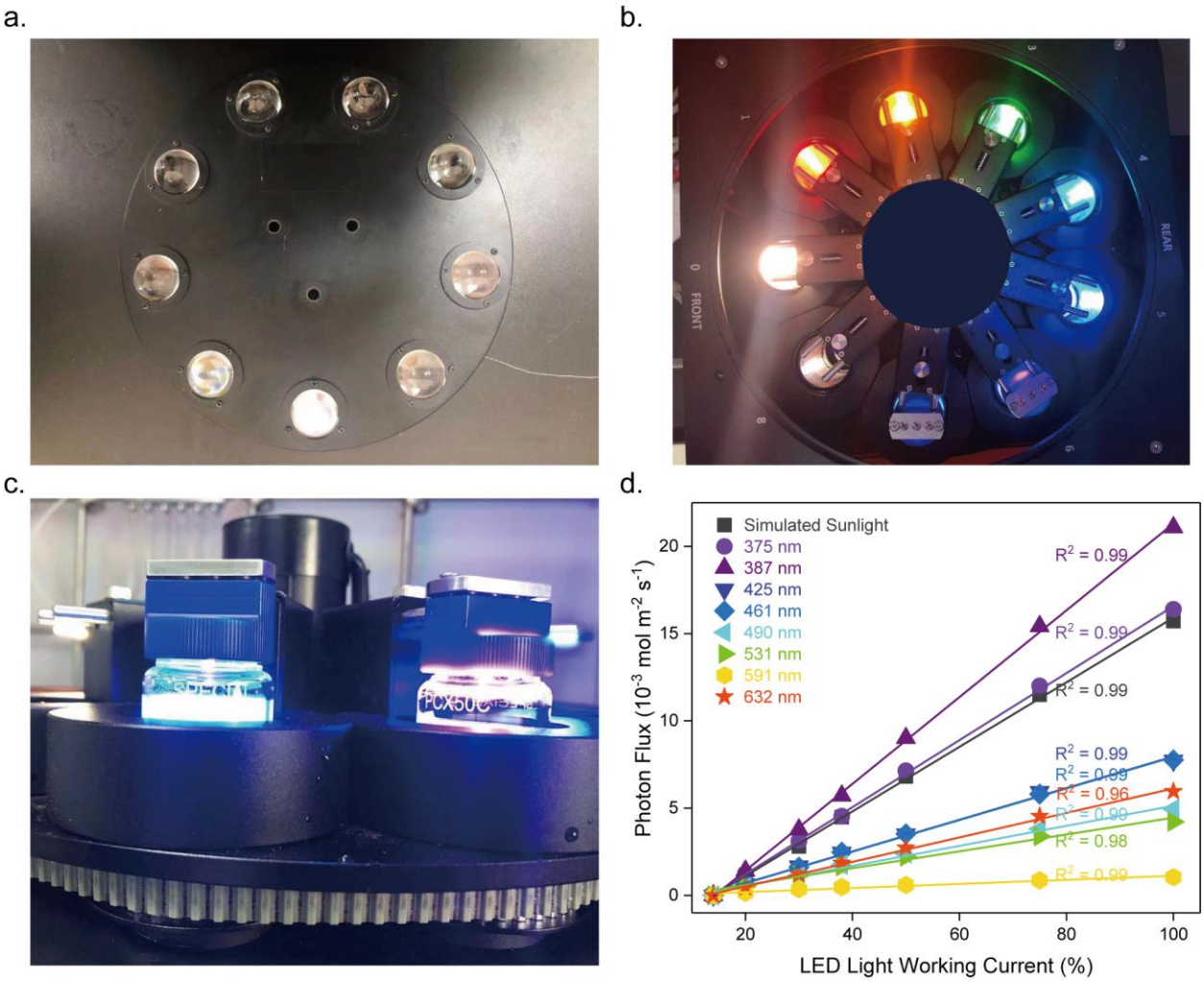

Figure S1. LED light reactor. (a)-(b) Custom-made LED light plate. (c) Side view of the quartz vial in the LED reactor under working conditions. (d) Tunable LED light intensity by controlling the working current. The 100% LED light working current correspond to 1 ampere current input. Error bars represent the standard deviation of LED light photon flux. When error bars are not visible, they are contained within the marker symbols.

Section S3 Sample analysis

Quantification of TMP

TMP was analyzed in an Agilent 1260 Infinity II high performance liquid chromatography (HPLC) coupled to a photodiode array detector (DAD). Over the course of the photolyses, 50 μL solution aliquots containing TMP were added to an LC vial with glass insert. Subsequently, 10 μL of each sample was injected into HPLC equipped with a C18 column (100 mm length × 3.0 mm i.d., 4.0 μm particle size) at 35°C. The mobile phase was methanol/water/0.02 M H_3PO4 (60:30:10, v/v/v) at a flow rate of 1.0 mL/min. The UV absorption at 280 nm was collected. TMP had a retention time of 1.57 min.

Quantification of FFA

Quantification of FFA was conducted following the similar method as TMP. Shortly, over the course of the photolyses, 50 μL solution aliquots containing FFA were added to an LC vial with glass insert. Subsequently, 10 μL of each sample was injected into an Agilent 1260 Infinity II HPLC equipped with a C18 column (100 mm length × 3.0 mm i.d., 4.0 μm particle size) at 35°C. The mobile phase was methanol/water/0.02 M H_3PO4 (30:60:10, v/v/v) at a flow rate of 1.0 mL/min. The UV absorption at 219 nm was collected. FFA had a retention time of 0.76 min.

Quantification of resorufin

Quantification of resorufin was conducted following the previously published analysis method.[3] 50 μL solution aliquots containing resorufin were added to an LC vial with glass insert. Subsequently, 10 μL of each sample was injected into an Agilent 1260 Infinity II HPLC equipped with a C18 column (100 mm length × 3.0 mm i.d., 4.0 μm particle size) at 35°C. The mobile phase was methanol/pH 7.4 sodium citrate buffer with 10% methanol (45:55, v/v) at a flow rate of 0.5 mL/min. The fluorescence of resorufin was measured by a fluorescence detector (FLR) at an excitation wavelength of 565 nm and an emission wavelength of 587 nm. Resorufin had a retention time of 1.34 min.

Quantification of hTPA

Briefly, 50 μL solution aliquots containing hTPA were added to an LC vial with glass insert. Subsequently, 20 μL of each sample was injected into an Agilent 1260 Infinity II HPLC equipped with a C18 column (100 mm length × 3.0 mm i.d., 4.0 μm particle size) at 35°C. The mobile phase was methanol/water/0.02 M H_3PO4 (30:60:10, v/v/v) at a flow rate of 1 mL/min. The fluorescence of hTPA was measured by a FLR detector at an excitation wavelength of 250 nm and an emission wavelength of 410 nm. hTPA had a retention time of 1.30 min.

Section S4. Spatial and temporal variations of solar light irradiance

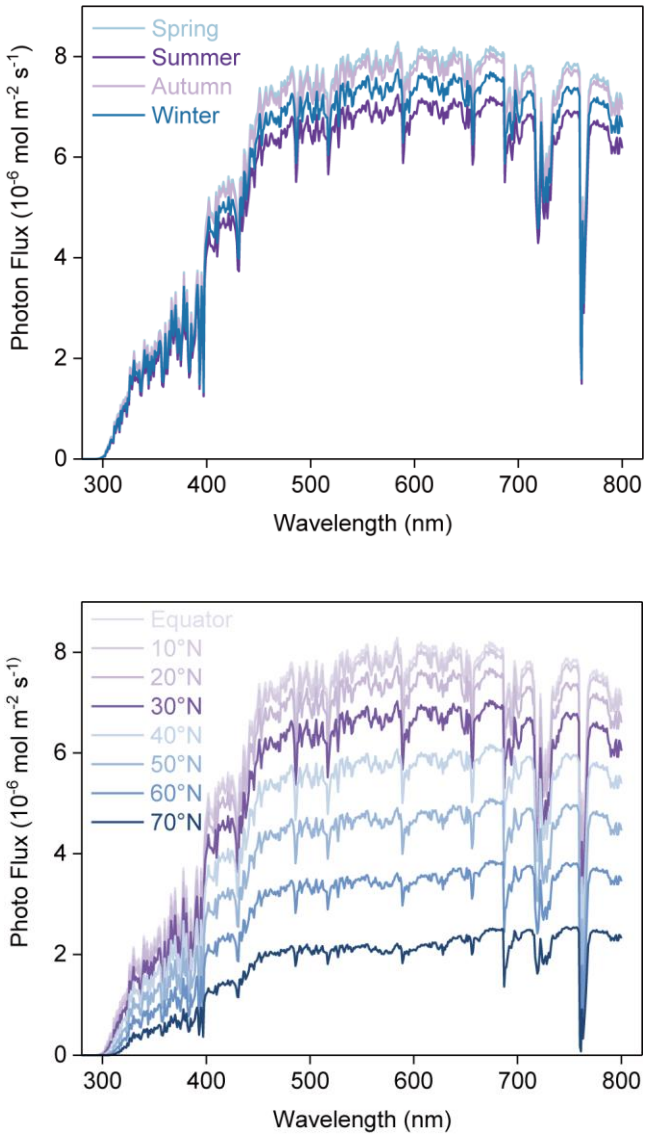

Figure S2. Sunlight spectrum at noon time with varying season (top, using equator as an example) and latitude (bottom, from equator to 70°N in spring as an example). Data were obtained from Apell and McNeill.[5]

Section S5. Input parameters of SMARTS

Table S1. Chosen inputs for SMATRS used for calculation of altitude mediated spectrum variation.

Parameter	Value
Site pressure	Latitude and height remain constant, with altitude varies from 0 to 5 km (0, 1, 2, 3, 4 and 5 km)
Atmosphere	Based on site temperature, relative humidity and season
Water vapor	Based on atmospheric temperature and relative humidity
Ozone	0.3341 (average of 10 reference atmospheres offered by SMARTS)
Gaseous absorption	Light pollution
Carbon dioxide	407 ppm
Extraterrestrial spectrum	Gueymard 2004
Aerosol model	Shettle & Fenn rural model
Turbidity	0.1
Albedo	0

Table S2. Chosen inputs for SMATRS used for calculation of AOD mediated spectrum variation.

Parameter	Value
Site pressure	Based on altitude, height and latitude
Atmosphere	Based on site temperature, relative humidity and season
Water vapor	Based on atmospheric temperature and relative humidity
Ozone	0.3341 (average of 10 reference atmospheres offered by SMARTS)
Gaseous absorption	Light pollution
Carbon dioxide	407 ppm
Extraterrestrial spectrum	Gueymard 2004
Aerosol model	Shettle & Fenn rural model
Turbidity	Varied from 0.1 to 1 (0.1, 0.2, 0.5, 0.8 and 1)
Albedo	0

Section S6. Assessment of UVA waveband on $^1O_2$ production

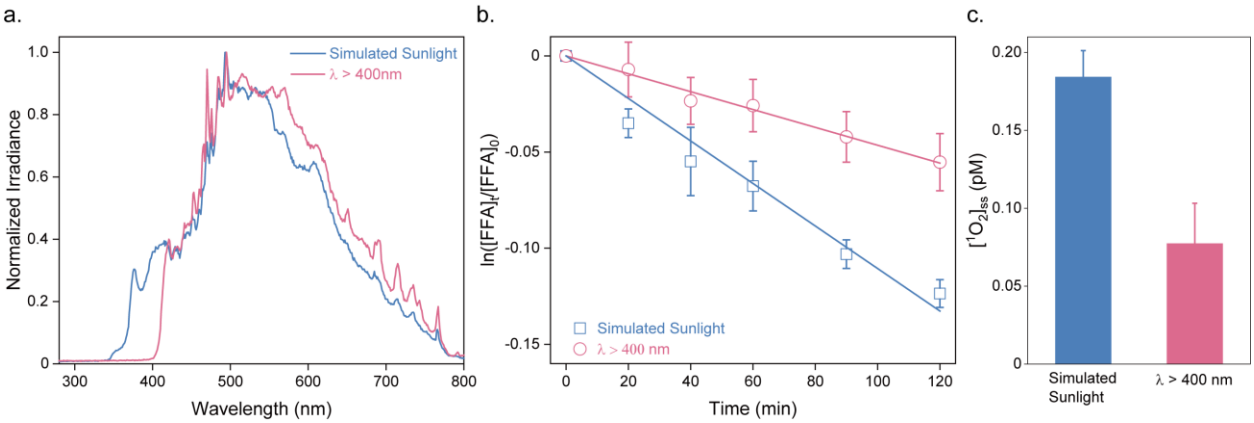

Figure S3. Contribution of UVA to $^1O_2$ production. (a) Xenon light spectra (simulated sunlight, blue line; filtered light (λ > 400 nm), pink line). (b) $^1O_2$-mediated transformation of FFA. (c) Steady-state concentrations of $^1O_2$.

Section S7. Prediction performance using the $^1O_2$ quantum yield spectrum

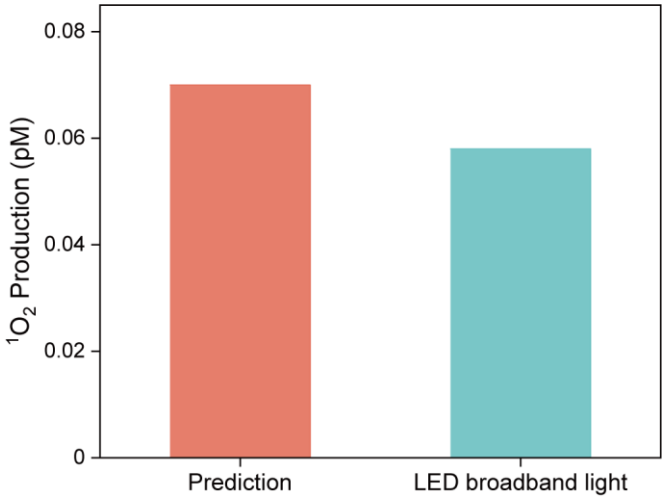

Figure S4. Comparison of $^1O_2$ production between prediction using $^1O_2$ quantum yield spectrum and experimental results.

REFERENCES

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