Supporting information

Photochemical Behavior of Microbial Extracellular Polymeric Substances in the Aquatic

Environment

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Authors Contributions

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Text S1 Chemicals and preparation of bacterial cultures.

Furfuryl alcohol (FFA, 98%), 2,4,6-trimethylphenol (TMP, 97%), terephthalate (TPA, 99%), 2-hydroxyterephthalate acid (HTPA, 97%), Folin agent and Methanol (99.9%) were purchased from Sigma-Aldrich, USA. Tetracycline hydrochloride (TC, 96%), tert-butyl alcohol (99.5%), 5,5-dimethyl-1-pyrroline-oxide (DMPO, 97%), and 2,2,6,6-tetramethylpiperidine (TEMP, 98%) were purchased from the Aladdin Co., China. All of the chemicals in this study were used as received without further purification. Sewage sludge was collected from a secondary sedimentation tank of the Lijiao municipal wastewater treatment plant in Guangzhou, China. Strains of *Shewanella oneidensis* MR-1 and *E. coli* were kindly provided by the Guangdong Institute of Eco-environment Science and Technology. The bacteria were activated and cultured for several generations in a typical Luria-Bertani medium containing 10 g tryptone, 5 g yeast extract, and 10 g NaCl in 1 L of water. The bacteria were incubated and horizontally shaken at 150 rpm (30 °C). The cultivated bacteria solutions were used for EPS extraction. Ultrapure water characterized as 18.25 MΩ·cm resistivity (produced by Unique-R20, RSJ Co. Ltd., China) was used in all of the experiments.

Text S2 Analysis of EPS compositions

The Bradford method was used to quantify the protein amounts in EPS with bull serum albumin (BSA) and Coomassie brilliant blue as the standard substance and color agent, respectively. The concentrations of proteins were determined by the absorbance at 595 nm, against standard curve of BSA.

Polysaccharides in EPS were determined using the phenol-sulfuric acid method with glucose as the standard substance. Generally, 5% phenol and sulfuric acid were mixed as a color agent with a volume ratio at 1:5, followed by cooling down in ice water. The samples were then mixed at ratio of 1:3 (v/v) with color agents before reading absorbance at 490 nm using a spectrophotometer.

Humic portions was measured using modified Lowry method with standard humic substances (obtained from the International Humic Substances Society) as the standard substance. Briefly, three color agents (A, B and C) were prepared separately as following. Solution A was prepared by dissolving 2 g Na₂SO₄ in 100 mL 0.1 mol/L NaOH solution and solution B was prepared by dissolving 0.05 g CuSO4 in 10 mL 10 g/L potassium sodium tartrate solution. Solution C was mixed by 50 mL solution A and 1 mL solution B right before experiments. Consequently, 4 mL Solution C and 1 mL sample solution was then fully mixed before adding 0.5 mL Folin agent. The absorbance at 750 nm was read using a spectrophotometer, denoted as A750. Another 1 mL sample was mixed with 4 mL solution A only, before adding 0.5 mL Folin agent. And absorbance of this solution was recorded at 735 nm, denoted as A735. Then, the humic substates in EPS was calculated as (A735-0.2*A750)/0.8.

Text S3 Fluorescence analysis of EPS

The excitation-emission matrix (EEM) spectra of variation for each EPS sample during five hours of illumination was recorded using the fluorescence spectrophotometer (FLS 1000). The EEM fluorescence spectra was scanned in an excitation range of 200-500 nm wavelengths and an emission range of 250-550 nm wavelengths, both at increments of 5 nm.¹

Text S4 Calculation of Steady-State Concentrations of Reactive Species.

Firstly, the [•OH]_{ss} quantification was based on the yield of targeting hydroxylation product (HTPA) from TPA.² The steady state •OH concentration was calculated as following:

•OH + TPA→2HTPA

 $\frac{d[2HTPA]}{dt} = \alpha \times k_{\bullet OH} \times [TPA][\bullet OH]ss$

Where α equals 35% as yield coefficient, $k_{\cdot OH}$ is 3.3×10^9 M⁻¹ s⁻¹ as the second-order constant between •OH and TPA.^{3,4}

The [1O2]ss was assessed by the decrease of selective probe agent, FFA. follows:

 $\frac{\mathrm{d}[\mathrm{FFA}]}{\mathrm{d}t} = -k_{1_{0_{2'}} \mathrm{FFA}} \times [\mathrm{FFA}][^{1}\mathrm{O}_{2}]_{\mathrm{ss}}$

Where $k_{1_{0,v} \text{ FFA}}$ is the second-order constant at $1.0 \times 10^8 \,\mathrm{M^{-1} \, s^{-1.3}}$

Similarly, the [³EPS*]_{ss} was quantified via decay kinetics of the probe compound, 2,4,6-trimethylphenol (TMP). Solutions in sealed reactor were sparged with nitrogen gas prior to the experiments. Calculation was guided by the equation below:

 $\frac{d[TMP]}{dt} = -k_{TMP, 3EPS*} \times [TMP][^{3}EPS*]_{ss}$

Where [TMP] is the initial concentration at 1 mM, $k_{\text{TMP}, 3_{\text{EPS}*}}$ is referred the rate constant between ³EPS* and TMP as 2 × 10⁹ M⁻¹ s^{-1.5}

Text S5 Sample extraction for FT-ICR MS analysis.

For the ESI FT-ICR MS analysis, 50 mL EPS solutions were acidified with HCl (grade of pro analysis, Merck, Germany) to pH 2.0 before flowing through a 6 mL Sep-pak C18 solid phase extraction cartridge (1 g sorbent per cartridge, Waters, U.S.A.). Note that the cartridge was previously activated by 18 mL diluted HCl solution (pH 2.0) and 18 mL methanol in succession. EPS solutions continuously flowed through the cartridges by gravity and subsequently the cartridges were flushed by pure nitrogen gas to fully remove water contents. Final samples were extracted by 6 mL methanol.

Calculations of weighted averaged (wa) values. The weighted averaged values were calculated according to the molecular formula deduced from FT-ICR MS analysis. Equations were given by Z. Yuan et al.⁶ and summarized below:

 $X/C_{wa} = \sum (X/C_i \times M_i)$

 $DBE_i = 1/2 \times (2 \times C + N - H + 2)$

 $DBE_{wa} = \sum (DBE_i \times M_i)$

 $M_i = I_i / \sum I_i$

where X represents the stoichiometric number of hydrogen (H), oxygen, nitrogen (N) and sulfur atoms in each formula, respectively. C represents the stoichiometric number of carbon. I_i is the peak magnitude per formula and M_i is relative magnitude.

Text S6 Determination of TC concentration and its transformation intermediates

The concentration of TC was determined by the HPLC (Essentia LC-16) with the Agilent column. The mobile phase was composed of 35% methanol and 65% ultrapure water (0.1% formic acid). The flow rate was fixed at 1 mL/min and the detection wavelength was 355 nm. The transformation products of TC during the illumination process were analyzed using ultra-performance liquid chromatography equipped with Q-Exactive hybrid Quadrupole-Orbitrap mass spectrometry (UPLC-Q-Orbitrap MS, Thermo Scientific, USA). A C18 column (4.6 mm × 150 mm, 4 μ m particle diameter, Agilent) was employed for separation. Samples were mixed with equal-voluminal methanol prior to injection in the UPLC-MS. The injection volume was 10 μ L. The mobile phase was comprised of 67% ultrapure water (0.1% formic acid), 22% acetonitrile, and 11% methanol at a flow rate of 0.3 mL/min. The MS analysis was performed under the following conditions: electrospray ionization source with a spray voltage of 3.5 kV and a capillary temperature of 300 °C. A full scan mode (50-1000 Da) at a mass resolution of 70000 was conducted. The MS data were further analyzed and possible transformed products were identified based on the parent compound using Compound Discoverer 2.0 (Thermo Scientific).

Text S7 No remarkable superoxide radicals (O₂⁻) was detected

In this work, the yield of superoxide radicals (O_2^{-}) was evaluated according to the procedures research.7,8 provided by previous Briefly, а probing agent of $O_2^$ named 2,3-bis(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-carboxanilide (XTT) was used at an initial concentration of 0.05 mM. The presence of O2- was determined by quantifying XTT derivates (XTT formazan) by UV-Vis spectroscopy at an absorbance wave length of 470 nm. Results showed that no remarkable O_2^- was detected in experiments. One explanation could be that the mineral-deficiency condition (mineral salts were excluded after dialysis) limited the generation of $O_2^{-.7}$ Generally, the generation of O_2^{-} is often attributed to the electron transfer between excited dissolved organic matters and oxygen.^{7, 9} However, the electron-transfer complex of organic and minerals was evidenced as indispensable pair for electron delivery during forming $O_2^{-,7,\ 10}$ Thus, it was the possible reason that few O_2^- could be detected during EPS illumination.

Text S8 The degradation of TC via direct photolysis

A degradation rate of 0.7 mg L^{-1} h⁻¹ was observed for the tetracycline via direct photolysis in this work. Though, some research might observe TC loss via direct photolysis, the initial TC concentration was 6.67 mg L^{-1} ,¹¹ which was only about one sixth of this work. It resulted in a TC photolysis rate of 1.5 mg L^{-1} h⁻¹ that was relatively comparable to our observation. This rate difference could be attributed to the different background solution and light intensity used in these studies. For instance, it reported TC has very low molar light absorptivity in neutral pH condition (i.e., our EPS solutions) while the water hardness (e.g., Ca^{2+} and Mg^{2+} ions) could significantly upgrade the direct photolysis of TC.^{11, 12} In our case, the metal ions (at least most of them) were removed from the EPS solution by dialysis, probably resulted in lower degradation of TC via direct photolysis. Nevertheless, the significant enhancement in TC phototransformation rate was still observed in the presence of EPS.

Peaks		Drobable exemples			
	S. oneidensis MR-1	E. coli	Sludge	riouaule examples	
				Humic	
А	350/450	350/450	350/450	acid-like/hydrophobic	
				acids	
В	275/310, 275/350	275/325, 275/360	275/310, 275/350	Tryptophan	
С	225/300		225/300	Aromatic Protein-like	
D	225/330		225/350	Tyrosine	
Е		230/425		Fulvic acids	
F		275/400, 300/410	275/400	Humic acid-like,	

Table S1 Identification principles of characteristic peaks in EEM spectra within three EPS samples.

Region I: Aromatic protein (C)

Region II: Aromatic protein II (D)

Region III: Fulvic acid-like (E)

Region IV: Soluble microbial by-product-like (B)

Region V: Humic acid-like (A and F)

	types					
NO.	Type of DOM	TOC (mg/L)	[•OH] _{ss} (10 ⁻¹⁷ M)	[³ Triplet*] _{ss} (10 ⁻¹⁵ M)	[¹ O ₂] _{ss} (10 ⁻¹³ M)	Ref.
1	EPS	20.0	2.55 - 8.73	3.01 - 4.56	2.08 - 2.66	This study
2	Effluent organic matter of a sewage plant	6.28	1.44 - 2.87	N/A ^a	2.75 - 6.97	13
3	Wastewater effluent	10.0	9.7	N/A	6.17	3
	Dissolved carbon from					
4	bamboo	14.46	N/A	N/A	14.6	7
	biochar					
	Dissolved carbon from					
5	bamboo	5.0	N/A	233	5.2	14
	biochar					

Table S2 Steady state concentrations of radical species compared with various DOM types

^aNot available

the Li b samples before and after manimation.							
Samples	Number of formulas	H/C _{wa}	O/C _{wa}	N/C _{wa}	S/C _{wa}	DBE/C _{wa}	
Raw M-EPS	508	1.409	0.356	0.024	0.039	7.620	
M-EPS after illumination	503	1.467	0.365	0.026	0.034	6.398	
Raw S-EPS	770	1.778	0.258	0.022	0.008	3.593	
S-EPS after illumination	631	1.781	0.278	0.026	0.012	3.134	
Raw E-EPS	555	1.659	0.289	0.022	0.016	5.149	
E-EPS after illumination	606	1.723	0.288	0.025	0.012	3.769	

Table S3 Profiles of intensity weighted averaged (wa) values for molecular composition of the EPS samples before and after illumination.



Scheme S1 Photogeneration of triplet intermediate, ${}^{1}O_{2}$, and •OH from EPS and their probing

reactions



Figure S1 Experimental setup of photochemical tests



Figure S2 The EEM spectra before and after illumination of (a) S-EPS, (b) M-EPS and (c) E-EPS, respectively. (The classification principles of I - V and A - F were detailed in Table S2)

It would be difficult to discuss which EPS sample might be superior for •OH generation since EPS could be both source and sink of •OH. In this case, the differences of chromophoric humic acids within three EPS samples were demonstrated, revealed by EEM-spectra (peak A in the EEM spectra). The steady-state of •OH was associated to some components in EPS such as humic substances.¹⁶ Enlightened by previous works on DOM, those humic parts were reported responsible for the •OH generation from DOM irradiation.^{17, 18} In this regard, lower humic concentration might bring lower •OH concentrations, which led to the results of lowest •OH concentrations in M-EPS samples.

The generation process of singlet oxygen was deduced from previous similar publications, based on the data we presented in our experiments. Briefly, the protein-like substances such as tryptophan, tyrosine (Tyr), and phenylalanine that identified in 3D-EEM spectra (Region I&II, and Table S1), are reported as light absorbers in the light wavelength range of 290-320 nm.¹⁹ Similarly, other research suggested that those aromatic amino acids could produce considerable amounts of ¹O₂ by photoexcitation.¹³ The process was also explained by Chin et al. that the ¹O₂ photoexcitation involves a series of reactions including photon adsorption and energy transfer, as following:²⁰

(1) Tyr +
$$hv \rightarrow {}^{1}Tyr$$

(2) ${}^{1}Tyr \rightarrow {}^{3}Tyr$
(3) ${}^{3}Tyr + {}^{3}O_{2} \rightarrow Tyr + {}^{1}O_{2}$

Therefore, it could be carefully deduced that those aromatic proteins might be responsible for ${}^{1}O_{2}$ generation from EPS.



Figure S3 EPR spectra of (a) DMPO-OH and (b) TEMP- ${}^{1}O_{2}$ adducts of three EPS samples. EPR experimental conditions: 20 mg (TOC)/L EPS and 100 mM DMPO or TEMP in ultrapure water solution, experiments were carried out at 30 °C after approximate 20 min simulated sunlight radiation. Spectra of blank groups (no EPS) were also presented.



Figure S4 (a) The effects of catalase (CAT) on the steady-state concentrations of hydroxyl radical. (b) Calculated contributions of two •OH formation pathways in three EPS solutions. Experiment conditions: [CAT] = 40 unit/L, [EPS] = 20 mg C/L, [TPA] = 1 mM.



Figure S5 The effects of high-energy triplets on apparent quantum yield of singlet oxygen. Percentages represent the contribution of high-energy triplets ($f_{\rm H}$ values) and error bars represent the standard deviations. Experimental conditions: 1 mM sorbic alcohol.



Figure S6 Comparisons of the yield of ³EPS*, [³EPS*]_{ss}, quamtum yield of ³EPS* in open-air or anaerobic conditions.

Actually, this measurement was operated advisedly in order to reveal the ability of triplets generation by EPS. In our cases, N_2 atmosphere was used to confirm an oxygen-deletion condition since oxygen might act as a triplet quencher causing inaccurate assessment of triplets steady-state concentration and quantum yields, as following:

 $\begin{array}{c} \text{Triplet} + \text{O}_2 \longrightarrow \text{EPS} + {}^1\text{O}_2 \\ \text{Excited} & \text{Ground} & \text{Ground} & \text{Excited} \\ \text{state} & \text{EPS} & \text{state} & \text{state} & \text{state} \end{array}$

As presented in the Figure S2, the yield of ${}^{3}EPS^{*}$, $[{}^{3}EPS^{*}]_{ss}$ under N₂ atmosphere were observed a little higher than that in open-air condition. The energy required for O₂ to ${}^{1}O_{2}$ was 94 kJ/mol, lower than that of most excited-state organic matter triplets for ${}^{1}O_{2}$ generation.¹⁵ Thus, O₂ was considered as a universal energy acceptor of most of organic triplet moieties. Based on that, it was quite challenging to evaluate and compare the $[{}^{3}EPS^{*}]_{ss}$ within three EPS samples in the presence of O₂. Considering this, we used a N₂ atmosphere in order to block the ${}^{3}EPS^{*}$ loss by O₂ quenching.



Figure S7 TOC removal efficiencies of three EPS solution after 5 h stimulated solar illumination (Initial TOC concentration: 20 mg/L).



Figure S8 Negative ion mass spectra of M-EPS obtained by FT-ICR MS before and after 5 h illumination.



Figure S9 (a) Van Krevelen diagrams of CHO, CHON, CHOS, CHONS of S-EPS compositions before and after illumination of simulated solar light, (b) the contribution of four major subcategories and (c) major classes of compounds seperated by black lines in Van Krevelen diagrams of two samples. (CRAM: carboxylic rich alicyclic molecules)



Figure S10 (a) Van Krevelen diagrams of CHO, CHON, CHOS, CHONS of E-EPS compositions before and after illumination of simulated solar light, (b) the contribution of four major subcategories and (c) major classes of compounds seperated by black lines in Van Krevelen diagrams of two samples. (CRAM: carboxylic rich alicyclic molecules)



Figure S11 Effects of scavengers on TC degradation by EPS/simulated solar light system. Experimental condition: [EPS] = 20 mg(TOC)/L, $[TC]_{ini} = 40 \text{ mg}/L$, $pH \sim 7.0$, $T \sim 30 \text{ °C}$, and [TBA] = 20 mM. The Blank group means EPS solution without any scavengers.



Figure S12 Fluorescence intensity (FI) changes of S-EPS in the presence of several radical quenchers. Experimental conditions: [TBA] = 20 mM, [EPS] = 20 mg/L, Temperature = 30 °C.

Some organic matters in EPS would be reactive to •OH or other radicals. For example, the proteins in EPS were reported as a significant sink of •OH. Therefore, the scavenging effects of EPS were generally tested here. As illustrated below in Figure S12, changes of fluorescent protein moieties via 3D-EEM spectra at a location of Ex/Em = 280/340 were followed. This location was mainly attributed to aromatic proteins as described in Section "*Composition Properties of the EPS Isolates Varied from Different Sources*". The tert-butyl alcohol (TBA) and N₂ were used for •OH quenching and blocking ${}^{1}O_{2}$ generation, respectively. The decrease of fluorescence intensity (FI) slowed down when quenchers were applied, indicated that parts of organic matter in EPS could experience decomposition by not only •OH but also ${}^{1}O_{2}$. It could be considered there was a dynamic balance between reactive species scavenging and generation and this balance eventually presented an increase in reactive species concentrations.



Figure S13 Mass spectra of (a) tetracycline and (b)~(f) identified photo-transformation products of tetracycline. Reaction conditions: 40 mg/L tetracycline and 20 mg (TOC)/L M-EPS solution at ~30 °C.



Figure S14 Proposed pathways of TC mediated by EPS under illumination.

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