Supplementary Material

Methyl bromide production from dissolved organic matter under simulated sunlight irradiation, and the important effect of ferric ions

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Text S1. The FTIR spectra of HA showed the typical bands for this type of material. Major bands were described as follows: -OH stretching vibration absorption at 3500-2500 cm^{-1}, C-H stretching vibration absorption of aliphatic series at 3000-2800 cm^{-1}, the band of asymmetric carboxyl groups near 1567 cm^{-1} and the symmetric COO– band around 1370 cm^{-1}, C-O stretching vibration in alcohols, ethers and/or polysaccharides around 1050-1165 cm^{-1}, skeleton vibration and stretching vibration of –C–C– at 900-1000 cm^{-1}. [1, 2]

Text S2. The addition of Fe(III) caused an obvious fluorescence quenching of the HA, indicating that Fe(III)-HA complexing reactions occurred, and the binding ability of HA and Fe(III) can be quantitatively described by the following equations:

$$\text{HA} + \text{Fe} = \text{HA–Fe}$$

$$K\text{c} = [\text{HA–Fe}]/([\text{HA}][\text{Fe}])$$

where [Fe] and [HA] are the concentrations of Fe(III) and organic ligands in HA, respectively, and K_C is the conditional stability constant for complex formation between Fe(III) and HA.

The K_C value can be estimated using the modified Stern−Volmer equation (1).

$$I_0/(I_0 - I) = 1/(fK\text{c}\,[\text{Fe}]) + 1/f$$

where I and I_0 are the fluorescence intensities of the samples with and without the addition of Fe(III), respectively, and f is the fraction of the initial fluorescence that corresponds to the binding fluorophores. The K_C value can be obtained from the slopes ($1/f\,K_C$) and intercepts ($1/f$) of the linear plots of $I_0/(I_0 - I)$ versus 1/[Fe].

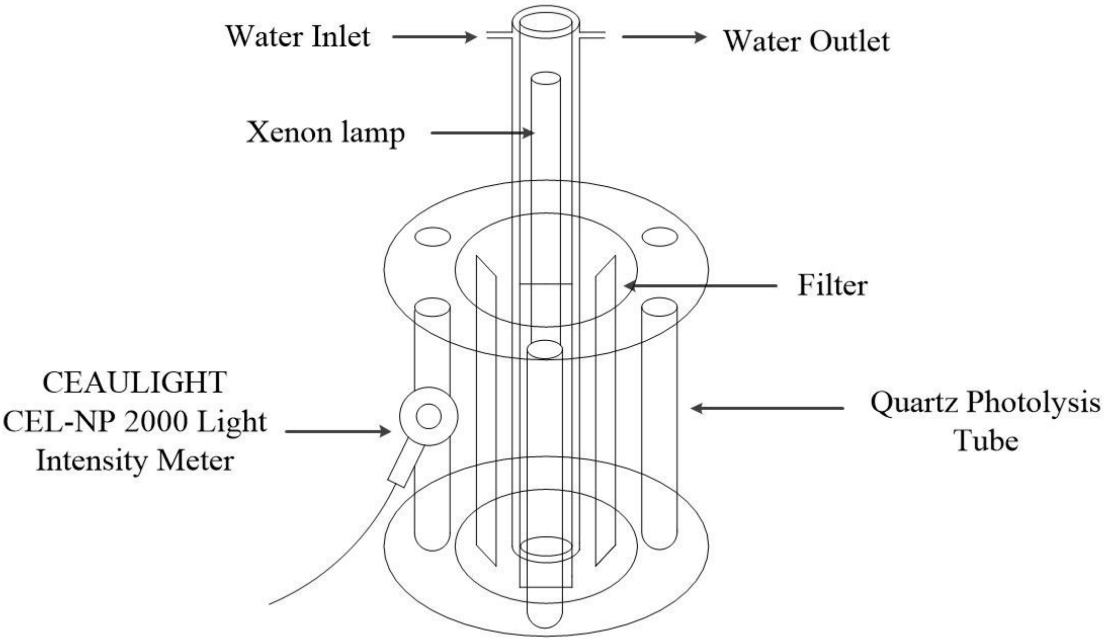

Fig. S1 Schematic of the device used for irradiation.

It is a so-called merry-go-round photoreactor. Xenon lamp was placed in a quartz jacket where cold water (10 °C) was driven by a cooling circulating pump to take away the heat of the infrared radiation. Eight pieces of filters were placed around the jacket to cut off the light with the wavelength below 290 nm. A light intensity meter (CEAULIGHT CEL-NP 2000) was used to measure the light intensity at the position where to place the quartz tubes.

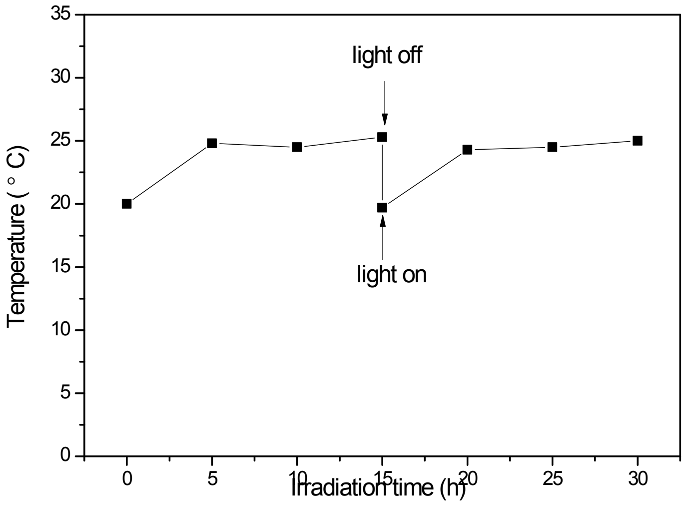

Fig. S2 Temperature changes of the reaction solutions during irradiation.

The initial temperature of the solution was about 20 °C. Light was turned on around 7:00 am, and turned off at 24:00 pm. The temperature of solutions rose to about 25 °C after 5 h irradiation and maintained around 25 °C during 15 h irradiation. Then the solution was placed at room temperature until next morning when the light was turn on again around 6:00 am.

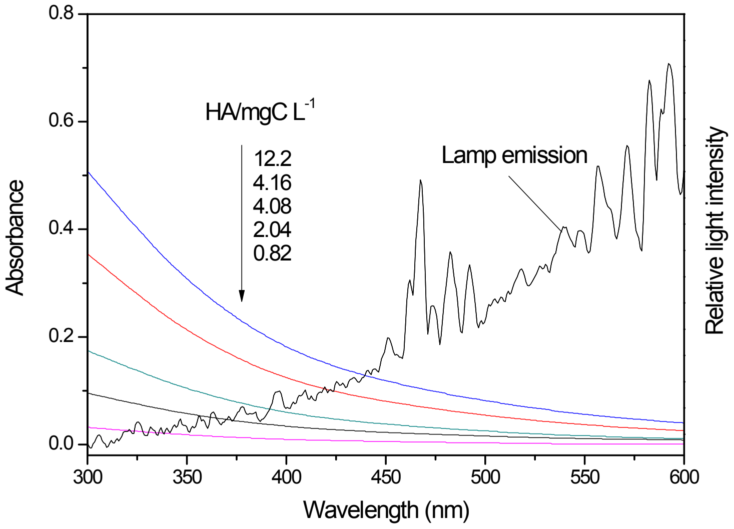

Fig. S3 HA absorption and Xenon lamp emission spectrum

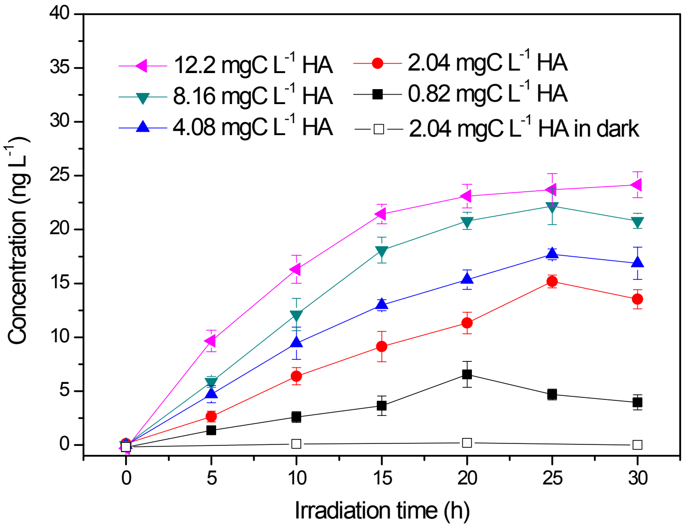

Fig. S4 Production of methyl bromide (corrected for light screening) in the presence of different concentrations of HA and 8 mmol L^{-1} Br^{-}.

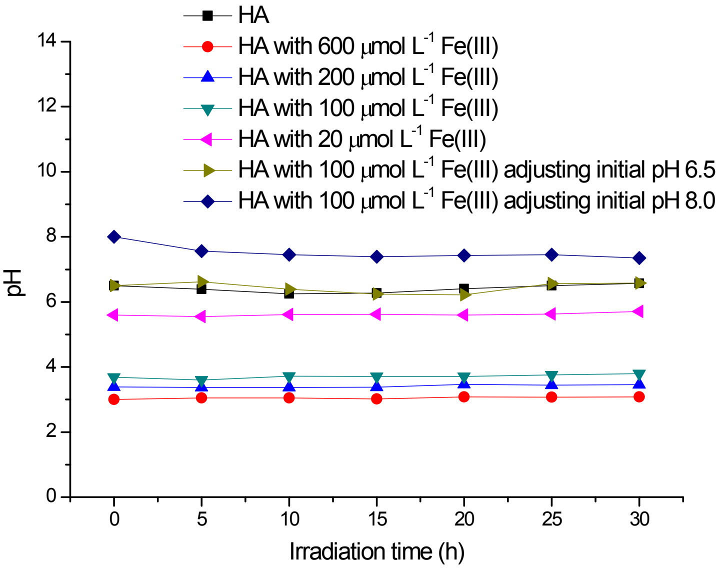

Fig. S5 Initial pH of the solutions containing different concentrations of Fe(III) and changes of pH during irradiation.

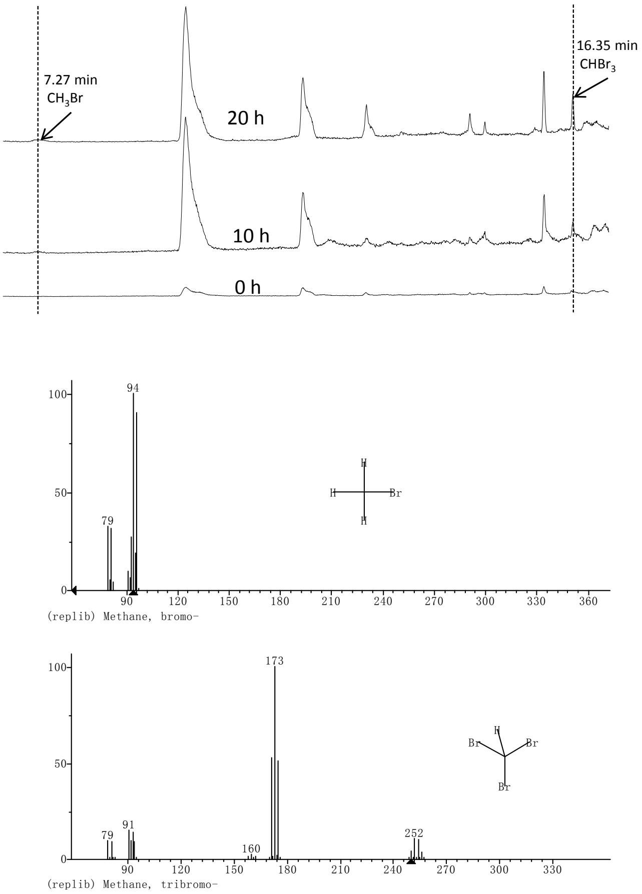

Fig. S6 Chromatogram of the gases from the solutions containing 2.04 mgC L^{-1} HA, 8 mmol L^{-1} Br^{-} and 100 μmol L^{-1} Fe(III) under irradiation of 0, 10 and 20 h, and the MS spectra of methyl bromide and tribromomethane.

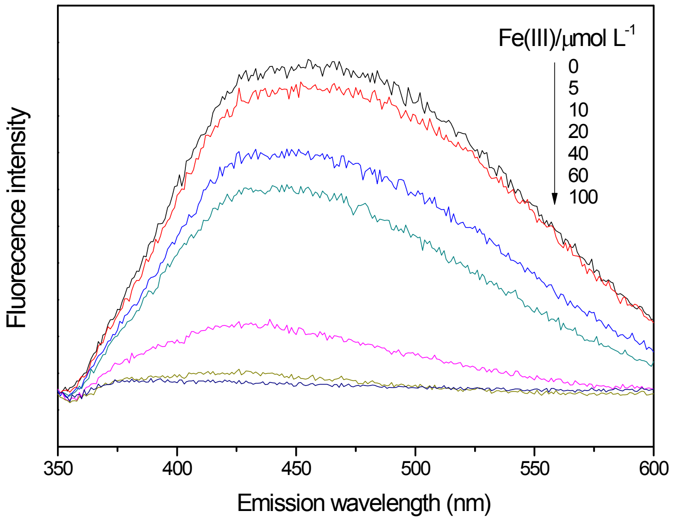

Fig. S7 Fluorescence emission spectra of HA in the presence of Fe(III). [HA]=8.16 mgC L^{-1}. The excitation wavelength was 320 nm, and the emission wavelength ranged from 350 nm to 600 nm.

Table S1 pH, TOC and concentrations of ions for the seawater

Parameters	Seawater
Cl^- (mM)	459
Br^- (μM)	683
SO_4^{2-} (mM)	23.8
TOC (mg C/L)	2.6
pH	8.0

The pH of seawater was measured by a pH-meter (Mettler Toledo, S40-K). The total organic carbon (TOC) concentration was determined by a TOC analyzer (Jena, Multi-N/C-2100S) after the water samples were acidified with 1 M HCl and purged with nitrogen. Concentration of Cl^-, Br^- and SO_4^{2-} was measured by a ThermoFisher ion chromatography (DIONEX ICS-5000).

Table S2 pH of the solutions containing different concentrations of Fe(III)

Fe(III) concentration (μmol L^{-1})	pH
0	6.5
20.0	5.6
100	3.7
200	3.4

600	3.0

Reference

(1) D. Wan, V. K. Sharma, L. Liu, Y. Zuo, Y. Chen, Mechanistic insight into the effect of metal ions on photogeneration of reactive species from dissolved organic matter. *Environ. Sci. Technol.,* 2019, **53**, 10, 5778-5786.