Supporting Information

Text S1

Briefly, 100 g peat soil was added into 1 L of 0.1 mol/L HCl solution, and the pH was adjusted to ~ 1.0. The suspension was shaken for 1 h, and then centrifuged at 6230 g for 10 min. The supernatant was discarded and the residue was neutralized to pH ~ 7.0 with 1.0 mol/L NaOH solution. After that, the treated sample was mixed with 1 L 0.1 mol/L NaOH solutions under a nitrogen atmosphere to extract humic and fulvic acids. The suspension was shaken for 4 h and settled overnight. The supernatant liquid was separated by centrifuging at 6230 g for 10 min and collected. The extracted HA was dialyzed against water and silver nitrate was used to test for removal of excess chloride ions. The resulting sample was stored as a homogenized freeze-dried powder. The fraction FA was passed in the resin XAD-8 in pH approximately 2 and washed with NaOH (0.1 mol/L). The precipitate was further treated by mixture solution of 0.1 mol/L HCl and 0.3 mol/L HF for 30 min to remove inorganic components, and then washed with de-ionized water for several times to obtain HM until acidity had been totally removed. The obtained samples were freeze-dried and stored in a desiccator with air-flow for more than three months.

Text S2

The XPS consisted monochromatic Al Kα radiation (180 W, 12 mA, 15 kV) and diameter beam spot of 500 mm. The pellets (2.0 mg of sample dispersed in 200 mg of KBr) were ground with an agate mortar before being pressed. FTIR spectra were recorded in the range of 4000–400 cm^{-1} with a 4 cm^{-1} resolution, and 64 scans were performed on each sample. To quantify the relative absorption intensity of each region of the carbon band, the spectra were baseline corrected and integrated with OMNIC 8.2 software.

Text S3

To identify the characteristics of EPFRs on HS samples, the operating parameters of the EPR instrument were as follows: X-band microwave frequency of 9.7 GHz, microwave power, 2.02 mW, center field, 3470 G; modulation amplitude, 4.0 G; sweep width, 200 G; receiver gain, 3.54×10^4; time constant, 41.0 ms; and sweep time, 167.7 s. Radical concentrations were calculated by comparing the signal peak area, as derived from $(\Delta H_{p\text{-}p})^2$ multiplied by the relative intensity. The chemical compound DPPH was put into a capillary and measured simultaneously with the respective HS sample, which was placed in a second capillary.

To detect the formation of ROS in the HS samples during the irradiation, EPR instrument parameters were adjusted as follows: center field, 3500 G; microwave power, 20 mW; sweep width, 200 G; sweep time, 30 s; and scan time, 2 min. The EPR spectra were simulated with the SpinFit and then the concentration of spin adducts were determined.

Table S1 Electron paramagnetic resonance (EPR) spectral characteristics of environmentally persistent free radicals (EPFRs) of humic substances (HS) after irradiation for 0 h and 2 h. (HA-CK: original humic acid; HA-2 h: humic acid samples after irradiation for 2 h; FA-CK: original fulvic acid; FA-2 h: fulvic acid samples after irradiation for 2 h; HM-CK: original humin; HM-2 h: humin samples after irradiation for 2 h.)

Samples	*g*-factor	Line width (G)	Concentration (10^{17}spins/g)
HA-CK	2.00339	4.94	0.59
HA-2h	2.00373	6.61	1.63
FA-CK	2.00349	6.18	0.20
FA-2h	2.00419	6.93	2.06
HM-CK	2.00307	4.75	0.86
HM-2h	2.00377	7.20	1.77

Table S2 Oxygen-containing functional groups analyzed by X-ray photoelectron spectroscopy (XPS) for humic substances (HS) after irradiation for 0 h and 2 h. (HA-CK: original humic acid; HA-2 h: humic acid samples after irradiation for 2 h; FA-CK: original fulvic acid; FA-2 h: fulvic acid samples after irradiation for 2 h; HM-CK: original humin; HM-2 h: humin samples after irradiation for 2 h.)

Samples	Chemical functions				
	C-(C,H)	C-O	C=O	O=C-O-O	C-O-O-H
HA-CK	0.09	0.18	0.05	-	-
HA-2h	0.08	0.07	0.13	-	-
FA-CK	0.08	0.10	0.07	0.05	-
FA-2h	0.03	0.08	0.09	0.05	-
HM-CK	0.09	0.15	0.07	-	0.03
HM-2h	0.08	0.13	0.08	-	0.06

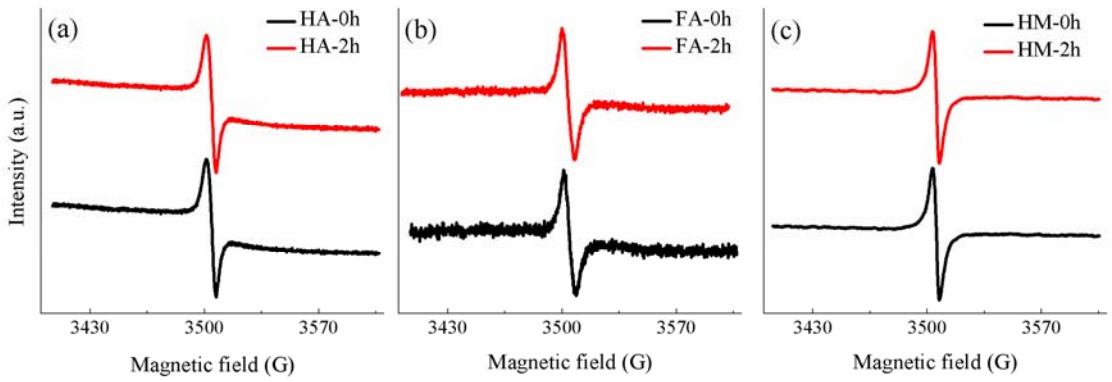

Fig. S1 Electron paramagnetic resonance (EPR) spectra obtained from original humic substances (HS) in dark conditions for 0 h and 2 h. (HA-0 h: humic acid in dark conditions for 0 h; HA-2 h: humic acid in dark conditions for 2 h; FA-0 h: fulvic acid in dark conditions for 0 h; FA-2 h: fulvic acid in dark conditions for 2 h; HM-0 h: humin in dark conditions for 0 h; HM-2 h: humin in dark conditions for 2 h.)

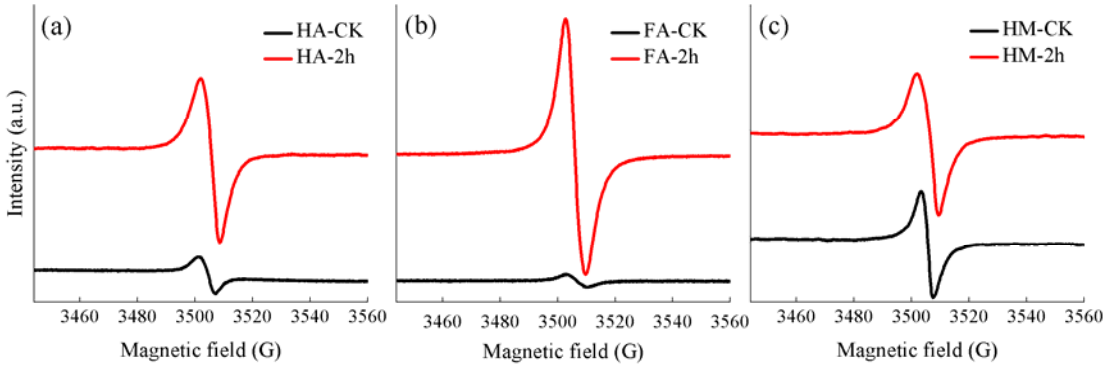

Fig. S2 Electron paramagnetic resonance (EPR) spectra of humic substances (HS) after irradiation for 0 h and 2 h. (HA-CK: original humic acid; HA-2 h: humic acid samples after irradiation for 2 h; FA-CK: original fulvic acid; FA-2 h: fulvic acid samples after irradiation for 2 h; HM-CK: original humin; HM-2 h: humin samples after irradiation for 2 h.)

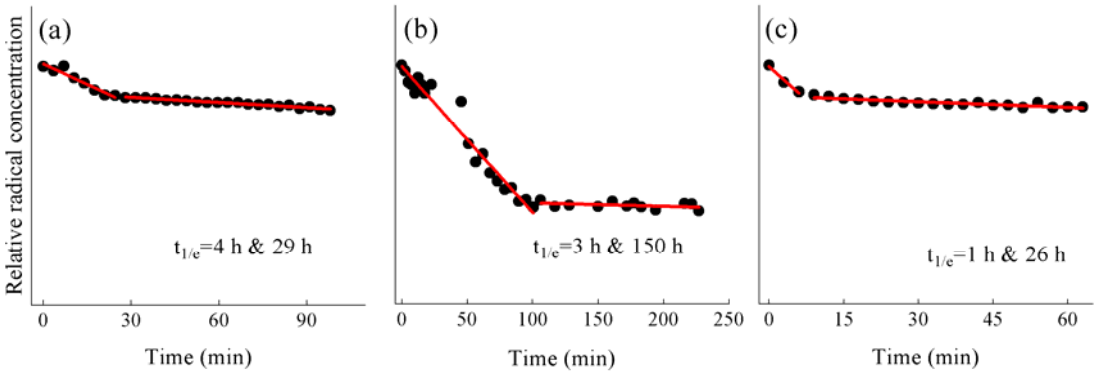

Fig. S3 First-order decay profiles of irradiated humic acid (a), fulvic acid (b) and humin (c) samples in dark conditions

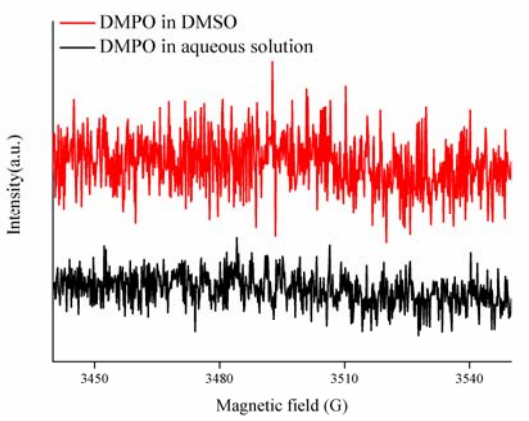

Fig. S4 Electron paramagnetic resonance (EPR) signal of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) in aqueous solution (black) and dimethyl sulfoxide (DMSO) (red) in dark conditions

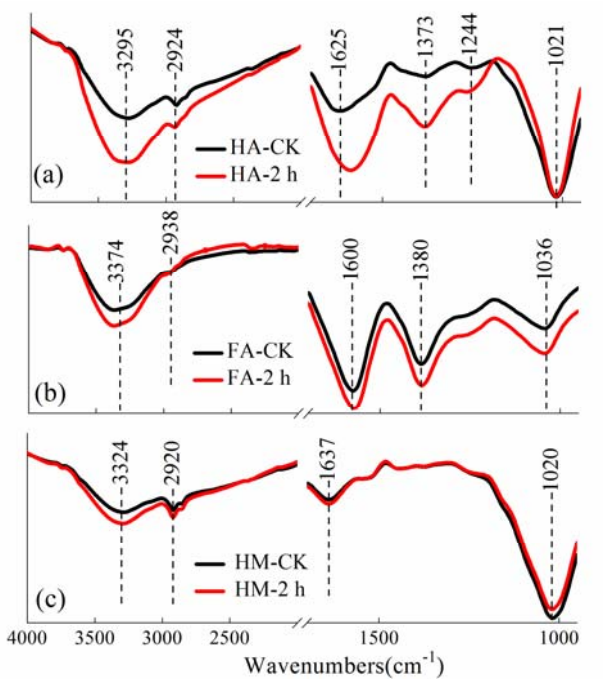

Fig. S5 Fourier transform infrared (FTIR) spectra of humic substances (HS) samples after irradiation for 0 h and 2 h. (HA-CK: original humic acid; HA-2 h: humic acid samples after irradiation for 2 h; FA-CK: original fulvic acid; FA-2 h: fulvic acid samples after irradiation for 2 h; HM-CK: original humin; HM-2 h: humin samples after irradiation for 2 h.)