Supporting Information for

Effect of different climate zone's humic and fulvic acid on aggregation of UV irradiated graphene oxide

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S1. Chemicals

5-Tert-butoxycarbonyl 5-methyl-1-pyrroline N-oxide (BMPO, ≥95%), 2,2,6,6-tetramethyl-4-hydroxy-piperidinyloxy (TEMP, ≥97%), 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO, ≥97%), and superoxide dismutase (SOD) were purchased from Sigma-Aldrich (St. Louis, MO, USA). J&K Co. LLC (Beijing, China) provided various chemicals like sodium hydroxide (NaOH), hydrochloric acid (HCl), hydrogen fluoride (HF), potassium chloride (KCl), potassium hydroxide (KOH) and sodium chloride (NaCl). All stock and working chemical solutions were made with deionized (DI) water obtained from Milli Q water purification system (resistance >18.2 MΩ). All chemicals of reagent or higher grade were used as received without any further purification.

S2. Sample pre-treatment and extraction of HA/FA

The extraction of HA and FA from the preserved samples were carried out by following the standard methodology of International Humic Substances Society (IHSS). The detailed procedure for isolation, purification and characterization of HA and FA was provided elsewhere (Ali et al., 2020). Briefly, the HA and FA was separated on the basis of solubility at different pH values. HA form precipitate at low pH (< 2) and can be easily separated from FA which is soluble in water at all pH values. HA was further purified by eliminating suspended solids and ash content by treating it with KOH/KCl and HCl/HF, respectively. Dialysis of HA with deionized water was carried out to remove Cl- ions. The FA in suspension was treated with XAD-8 resin and 0.1 M NaOH was used to extract FA. Finally, the H+ resin was used to remove Na+ and fraction was freeze dried. The different techniques applied for characterization of HA and FA were described in our previous study Ali et al. (2020).

S3. GO characterization

The physical structure and morphology for small and large GO was detected by S-4800/EX-350 field emission transmission electron microscopy (SEM, Hitachi, Tokyo, Japan) at acceleration voltage of 5 kV. To measure the crystallinity and interlayer distance of small and large GO in dark and UV irradiation condition, the X-ray diffraction (XRD) technique was used. X-ray diffractometer (Smart-Lab, Rigaku, Tokyo, Japan) was used for sample scanning over range of 2θ = 5-80° with Cu $K\alpha$ radiation at 40 kV and 40 mA. Functional groups of small and large GO compressed with potassium bromide (KBr) pellets before and after UV irradiation were observed by Fourier Transform infrared spectrometer (FTIR NEXUS 670, OSIC, USA). The dried powder of small and large GO was used to detect XPS spectra using an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Scientific Ltd, East Grinstead, England). The radiation source of Al $K\alpha$ at 1486.6 eV, takeoff angle of 0 degree, and 30 eV of pass energy was adjusted for XPS analysis. The peak at 284.6 eV (C1s) was used to calibrate the surface charge effects. Hydrodynamic diameter (D_h), zeta potential (Z-potential), and particle size distributions (PSDs) of small and large GO were detected with dynamic light scattering (DLS) machine (Brookhaven Instruments Corporation, New York, USA).

S4. Particle size distribution of GO (small and large) in DI water

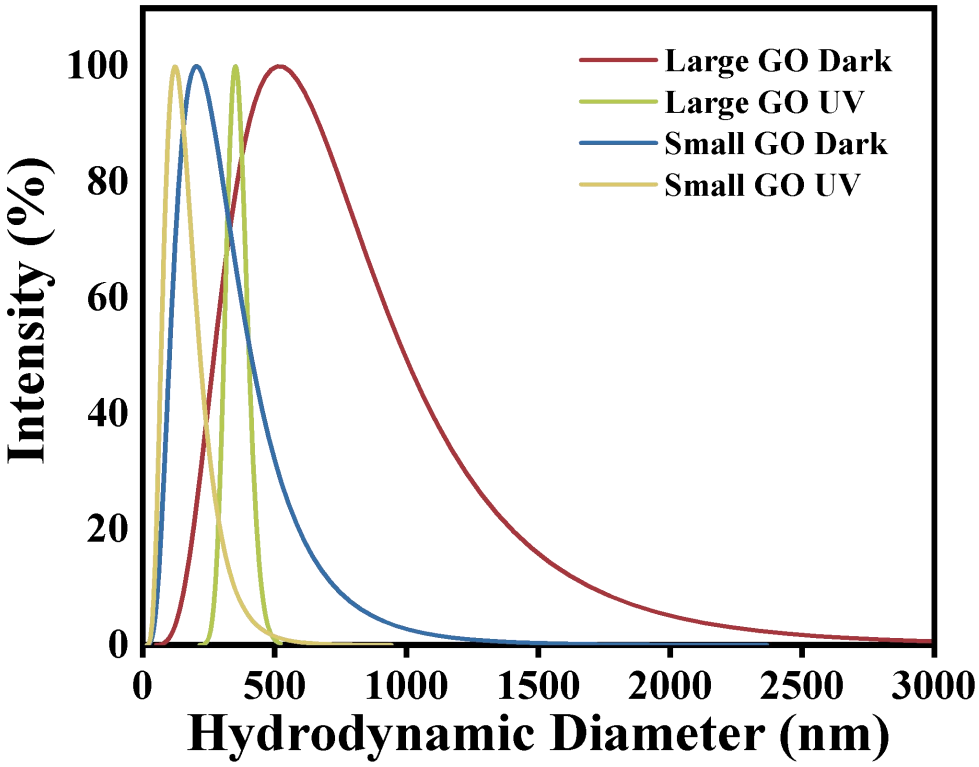

Fig. S1 Particle size distribution of small and large GO in DI water before and after 2 h UV irradiation.

S5. ROS (BMPO spin adducts) generation of GO with/without HA/FA

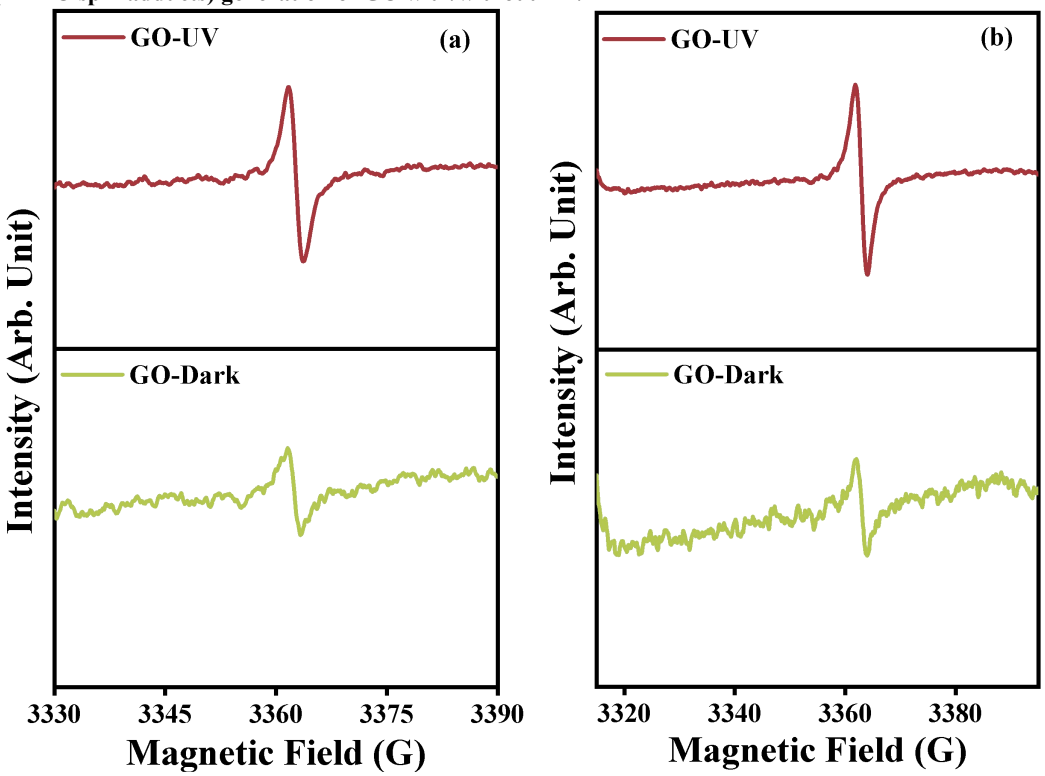

Fig. S2 BMPO adduct with •OH/ $O_2^{\bullet-}$ (a) and BMPO adduct with •OH/ $O_2^{\bullet-}$ in the presence of SOD (b) of pristine and UV irradiated GO.

S6. XPS survey of C1s and O1s regions of dark and UV irradiated small and large GO

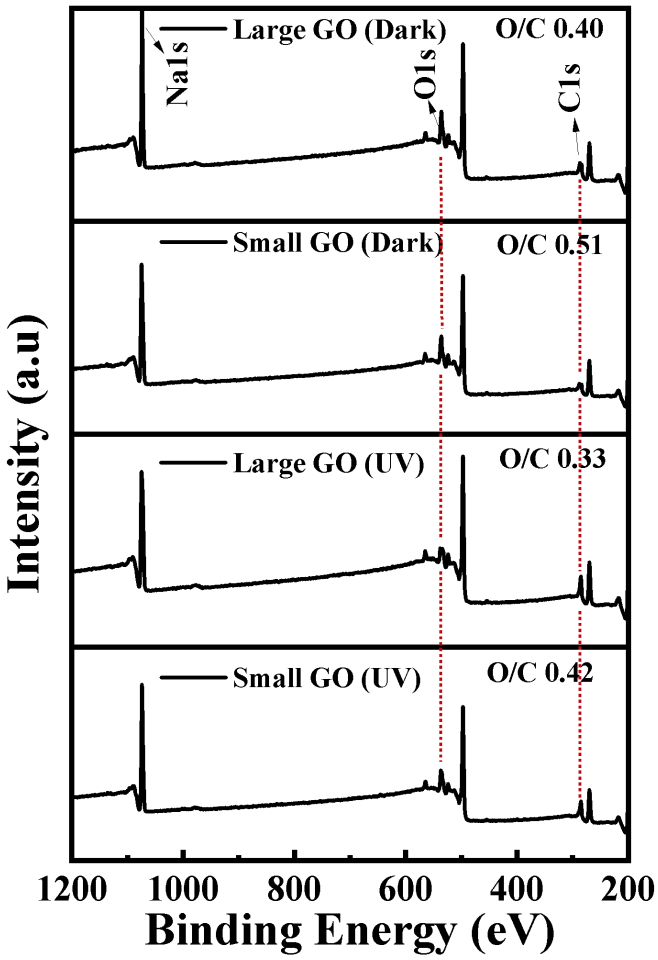

Fig. S3 XPS survey of C1s and O1s regions of dark and UV irradiated small and large GO.

S7. DLVO interaction energy of small and large GO

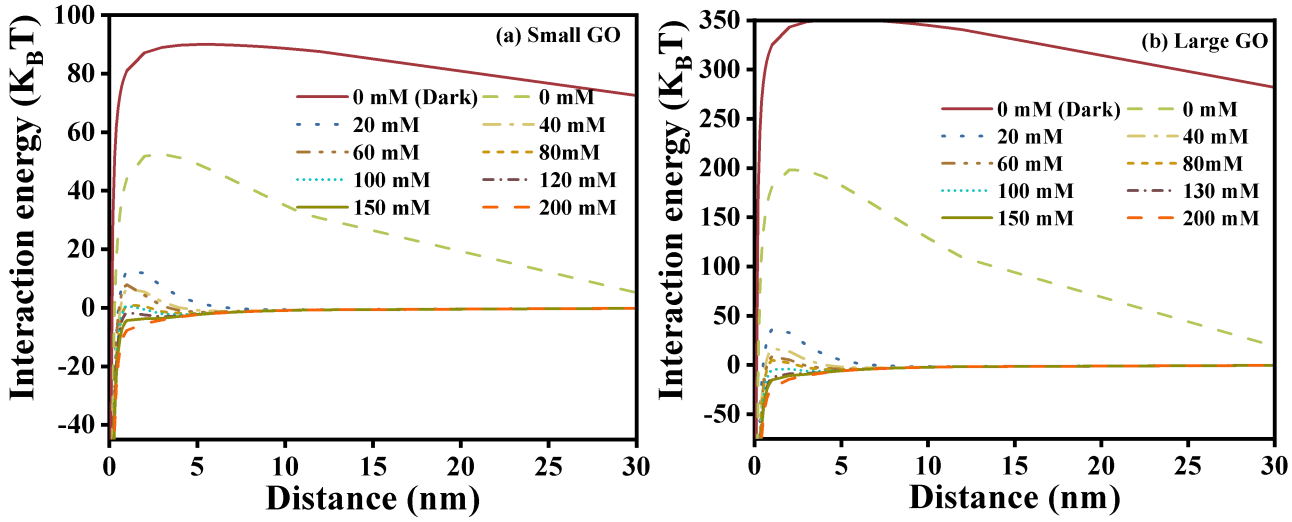

Fig. S4 DLVO interaction energy as a function of the separation distance between two interacting small GO (a) and large GO (b) in different concentrations (0 – 200 mM NaCl) of NaCl solutions under dark and UV irradiated GO.

S8. Z-potential of small and large GO before and after UV irradiation

Table S1 Z-potential (mV) of small and large GO before and after 2h UV-light irradiation

DOM (mg·C/L)			NaCl (mM)	Small GO		Large GO	
				Before UV	After UV	Before UV	After UV
Panjin	HA	0.2	200	-24.30	-23.79	-22.82	-22.02
		1.0		-25.31	-24.25	-24.11	-23.53
	FA	0.2		-22.65	-20.67	-21.22	-19.97
		1.0		-23.25	-22.56	-22.11	-21.87
Tang Ke	HA	0.2		-25.37	-22.96	-24.33	-21.12
		1.0		-26.66	-23.35	-26.37	-22.44
	FA	0.2		-25.66	-22.66	-22.27	-21.97
		1.0		-25.18	-25.35	-24.95	-23.22
Maqin	HA	0.2		-21.94	-21.08	-21.52	-19.26
		1.0		-23.50	-21.77	-22.17	-20.17
	FA	0.2		-29.28	-27.34	-27.16	-26.13
		1.0		-27.33	-28.32	-27.91	-27.36
Makou	HA	0.2		-30.31	-30.94	-30.47	-29.52
		1.0		-32.47	-33.03	-33.03	-31.44
	FA	0.2		-22.05	-19.00	-21.93	-17.53
		1.0		-23.37	-23.34	-23.44	-20.93
No			0	-34.10	-33.14	-39.76	-41.22
			30	-26.18	-29.49	-29.06	-27.02
			50	-24.67	-24.08	-20.38	-24.73
			70	-26.57	-26.08	-21.07	-24.06
			80	-23.16	-25.45	-22.53	-23.70
			90	-21.87	-24.25	-25.56	-21.66
			100	-23.95	-22.94	-22.10	-24.55
			130	-23.60	-25.92	-20.72	-18.84
			150	-22.23	-23.86	-26.61	-20.89
			200	-20.63	-18.11	-23.75	-20.61

S9. % functional groups of small and large GO

Table S2 The % functional groups of small and large GO before and after UV irradiation**.**

Sample	Condition	C-C/C=C	C-O	C=O
Small GO	Dark	52.82	31.96	15.21
	UV	63.91	23.02	13.07
Large GO	Dark	52.93	32.28	14.79
	UV	61.44	25.64	12.92

References

Ali J, Li Y, Wang X, Zhao J, Xi N, Zhang Z, Xia X (2020). Climate-zone-dependent effect mechanism of humic acid and fulvic acid extracted from river sediments on aggregation behavior of graphene oxide. Science of the Total Environment, 721: 137682