

**Electronic supplementary information for**

**Effects of ozone and produced hydroxyl radical on the transformation of graphene oxide in  
aqueous media**

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### **S1.0 Preparation of RGO**

To prepare RGO,  $\text{N}_2\text{H}_4$  (1 mL) was added slowly to 400 mL of a 250 mg/L GO suspension. Next, the mixture was heated to 80°C under vigorous stirring for 24 h. Afterward, the suspension was cooled to room temperature, and filtered through 0.22  $\mu\text{m}$  membrane filters. The RGO material retained on the filter was collected and added to approximately 200 mL DI water, and ultrasonicated at 100 W for 30 min. The rinsing procedure was repeated three times. Finally, the suspension was filtered through 0.45  $\mu\text{m}$  membrane filters to remove large RGO aggregates.

### **S2.0 Mass spectrometry**

Aqueous GO and GO<sub>2</sub>O<sub>3</sub> samples were passed through 0.22  $\mu\text{m}$  filters. The filtrates were collected and 3  $\mu\text{L}$  aliquot collected from each filtrate was analyzed using UPLC–MS/MS (UPLC–Xevo TQ-S, Waters, USA). The UPLC was equipped with a Waters C18 (4.6  $\times$  150 mm) column, which was eluted with gradient solvent from 90:10 (v/v) to 100:0 (v/v) H<sub>2</sub>O/acetonitrile with 0.1% formic acid at a flow rate of 0.40 mL/min. The full scan data was acquired from  $m/z$  100-1000 in positive ion mode for 14 min.

### **S3.0 Measurement of $K_{\text{DW}}$**

Samples were prepared by adding 4 mL of GO or GO<sub>2</sub>O<sub>3</sub> suspension to a test tube containing 1 mL of *n*-dodecane. The test tube was vortexed for 2 min, and then left undisturbed for 15 min to allow phase separation.  $K_{\text{DW}}$  was assessed as the fraction of GO or GO<sub>2</sub>O<sub>3</sub> that partitioned into *n*-dodecane from the aqueous phase.

### **S4.0 Adsorption isotherm experiments to GOs**

The GO and GO<sub>2</sub>O<sub>3</sub> were added to a series of 20 mL amber glass vial to give a final concentration of 50 mg/L GO in the working suspensions. Next, the suspension was spiked with a test compound (in methanol). The pH was unadjusted for the phenanthrene experiments (to maintain a constant ionic strength among different treatments). For 1-naphthol, the pH of the suspensions was adjusted to 7 (using a NaH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub> buffer) to ensure that 1-naphthol was in the non-ionized form. The suspensions of contaminant, GO or GO<sub>2</sub>O<sub>3</sub> were equilibrated for 7 d by tumbling at 8 rpm in the dark. Then, fibers were added to the suspensions and allowed to equilibrate for 30 d (for phenanthrene) or 7 d (for 1-naphthol). Finally, the fibers were taken out, wiped with a wet tissue, and extracted with methanol to analyze the mass of the compound on the fiber. The aqueous solution was diluted with methanol to analyze the concentration of the compound in the dissolved phase. The sorption data were fitted with the linear sorption isotherm:  $C_{\text{fiber}} = K_{\text{fiber}} \cdot C_e$ , where  $C_{\text{fiber}}$  (mg/L) and  $C_e$  (mg/L) are the equilibrium concentrations of a compound on the fiber and in the solution, respectively;  $K_{\text{fiber}}$  (L/L) is the fiber-water distribution coefficient. All the adsorption experiments were carried out at room temperature.

**Table S1.** Energy dispersive X-ray spectroscopy (EDS) analysis of GO before and after ozone treatment (n = 3)

Parallel sample	GO		GO_O <sub>3</sub>	
	C (at%)	O (at%)	C (at%)	O (at%)
1	67	33	58	42
2	65	35	62	38
3	65	35	59	41
O/C ratio (Avg. ± SD)	0.53 ± 0.03		0.68 ± 0.06	

**Table S2.** Summary of the O-containing functional groups of RGO, graphene and graphite obtained from X-ray photoelectron spectroscopy.

Sample <sup>a</sup>	C <sup>b</sup> (at%)				total C <sup>b</sup> (at%)	total O <sup>b</sup> (at%)	O/C ratio <sup>b</sup>
	C–C/ C=C	C–O–C/ C–OH	C=O	O–C=O			
RGO	58	15	ND <sup>c</sup>	5	78	14	0.18
RGO_O <sub>3</sub>	43	18	2	6	69	23	0.35
Graphene	74	13	ND <sup>c</sup>	4	91	9	0.10
Graphene_O <sub>3</sub>	53	17	2	5	77	21	0.27
Graphite	99	ND <sup>c</sup>	ND <sup>c</sup>	ND <sup>c</sup>	99	1 <sup>d</sup>	0.01
Graphite_O <sub>3</sub>	74	9	2	2	87	13	0.15

<sup>a</sup> RGO represents reduced GO; the term “O<sub>3</sub>” indicate ozonation to carbon-based materials.

<sup>b</sup> Analyzed with X-ray photoelectron spectroscopy.

<sup>c</sup> ND = not detected.

<sup>d</sup> Interference of impurities.

**Table S3.** O-containing functional groups of GO upon ozonation with and without t-BuOH obtained from X-ray photoelectron spectroscopy.

Sample <sup>a</sup>	C <sup>b</sup> (at%)				total C <sup>b</sup> (at%)	total O <sup>b</sup> (at%)	O/C ratio <sup>b</sup>
	C-C/ C=C	C-O-C/ C-OH	C=O	O-C=O			
GO	37	19	5	3	66	33	0.50
GO_O <sub>3</sub>	26	21	7	6	60	38	0.63
GO_O <sub>3</sub> _t-BuOH	47	18	6	3	74	27	0.36

<sup>a</sup> The term "O<sub>3</sub>" indicate ozonation.

<sup>b</sup> Analyzed with X-ray photoelectron spectroscopy.

**Table S4.** O-containing functional groups of graphite upon ozonation with and without t-BuOH obtained from X-ray photoelectron spectroscopy.

Sample <sup>a</sup>	C <sup>b</sup> (at%)				total C <sup>b</sup> (at%)	total O <sup>b</sup> (at%)	O/C ratio <sup>b</sup>
	C–C/ C=C	C–O–C/ C–OH	C=O	O–C=O			
Graphite	99	ND <sup>c</sup>	ND <sup>c</sup>	ND <sup>c</sup>	99	1 <sup>d</sup>	0.01
Graphite_O <sub>3</sub>	74	9	2	2	87	13	0.15
Graphite_O <sub>3</sub> t-BuOH	98	ND <sup>c</sup>	ND <sup>c</sup>	ND <sup>c</sup>	98	2 <sup>d</sup>	0.02

<sup>a</sup> The term “O<sub>3</sub>” indicate ozonation.

<sup>b</sup> Analyzed with X-ray photoelectron spectroscopy.

<sup>c</sup> ND = not detected.

<sup>d</sup> Interference of impurities.

**Table S5.** Selected properties of suspensions of GO and O<sub>3</sub>-treated GO under different solution chemistry conditions.

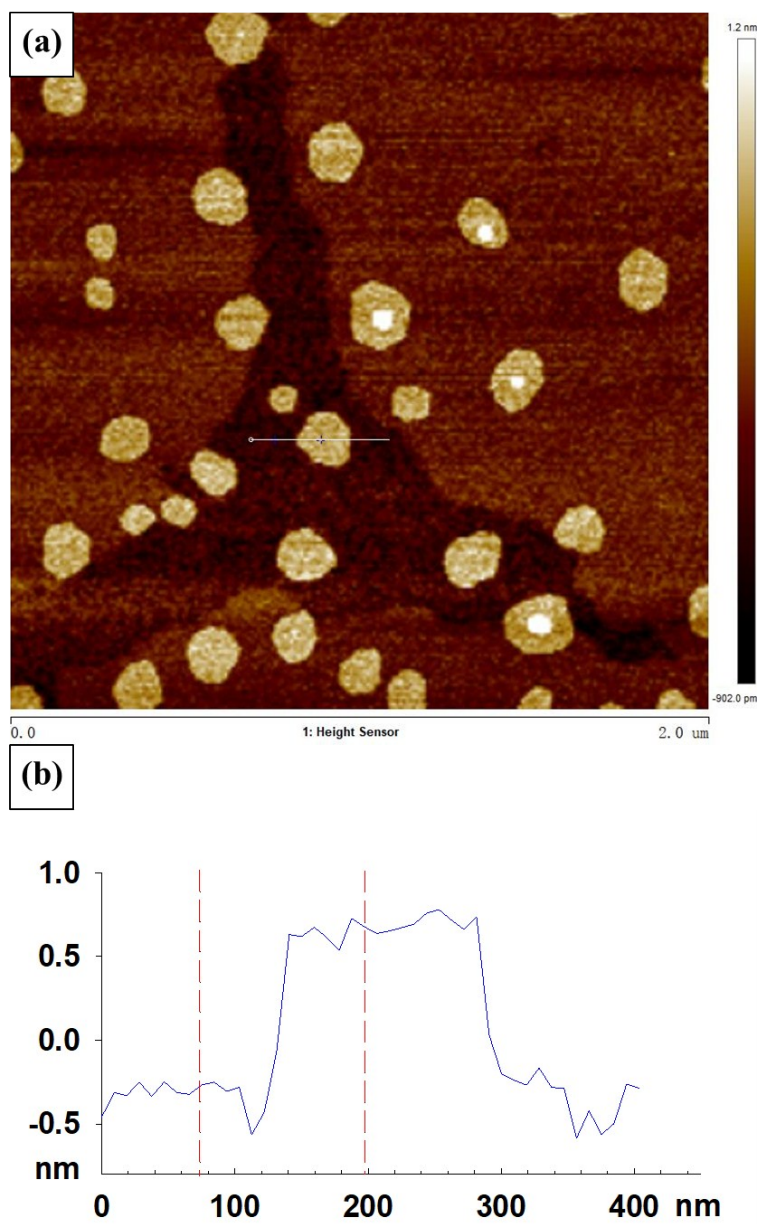
Sample	Ionic Strength	pH	$Z_{ave}^a$ (nm)
GO	35 mM NaCl	6.0	186.0
GO_O <sub>3</sub>	35 mM NaCl	6.0	120.2
GO	0.3 mM CaCl <sub>2</sub>	6.0	353.7
GO_O <sub>3</sub>	0.3 mM CaCl <sub>2</sub>	6.0	124.8

<sup>a</sup> Hydrodynamic diameter of GOs nanoparticles based on dynamic light scattering analysis.

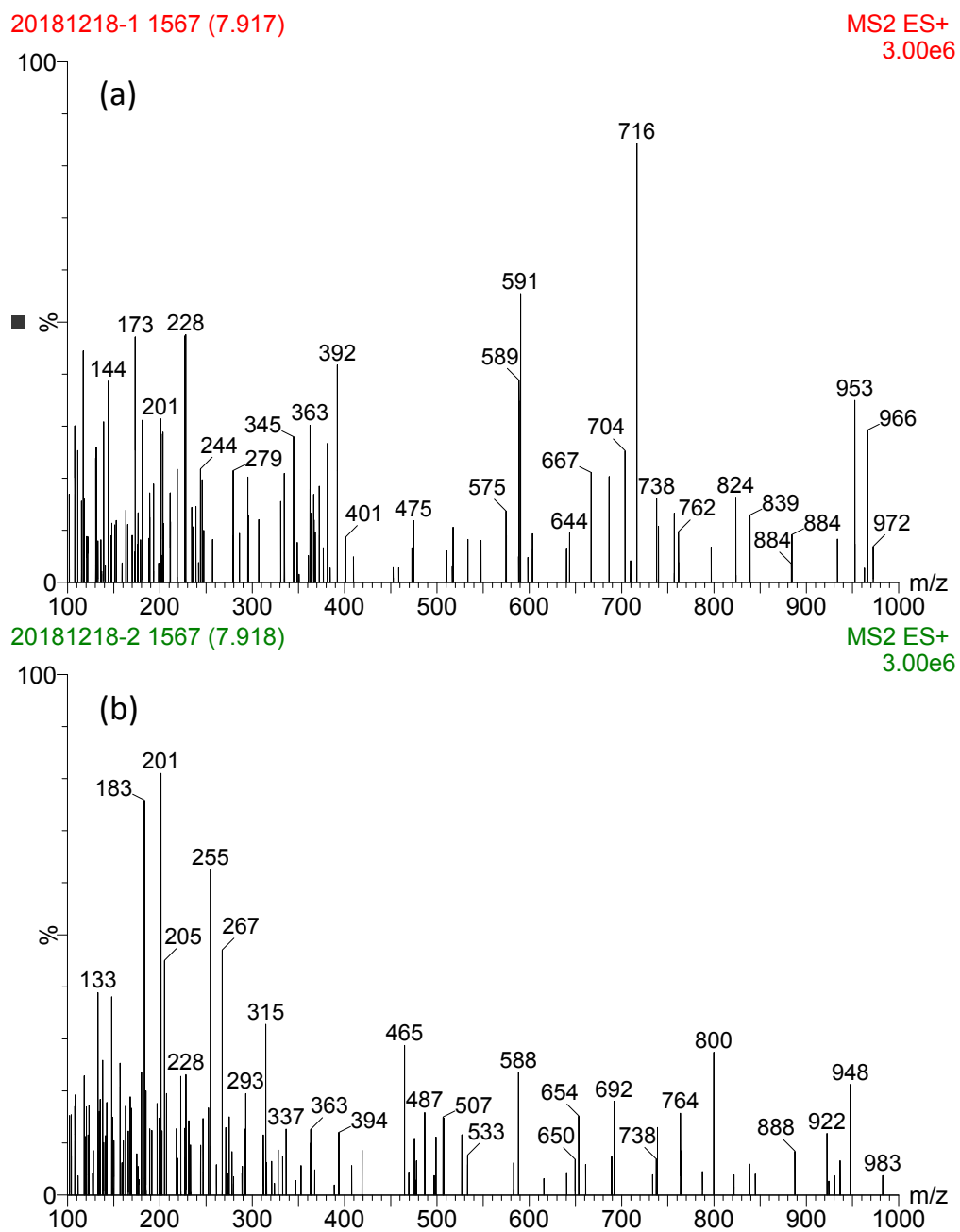


**Table S6.** Summary of adsorption parameters [Freundlich model coefficients ( $K_F$  and  $n$ )] of phenanthrene and 1-naphthol to GOs.

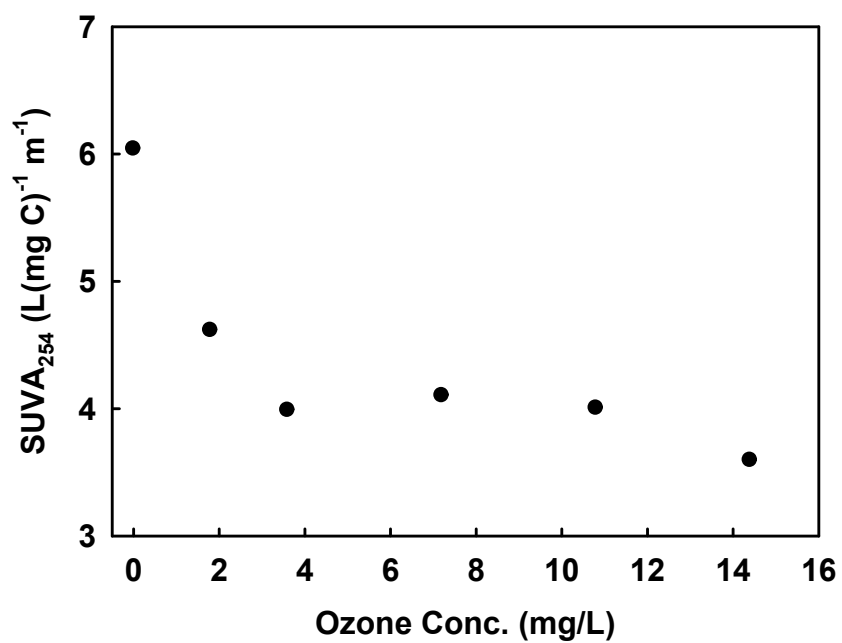
Adsorbate	GOs	$K_F$ ( $\text{mg}^{1-n}\text{L}^n/\text{kg}$ )	$n$	$R^2$
Phenanthrene	GO	78796	0.7721	0.998
Phenanthrene	GO_O <sub>3</sub>	54634	0.7975	0.998
1-Naphthol	GO	39317	0.3888	0.985
1-Naphthol	GO_O <sub>3</sub>	16501	0.6664	0.928



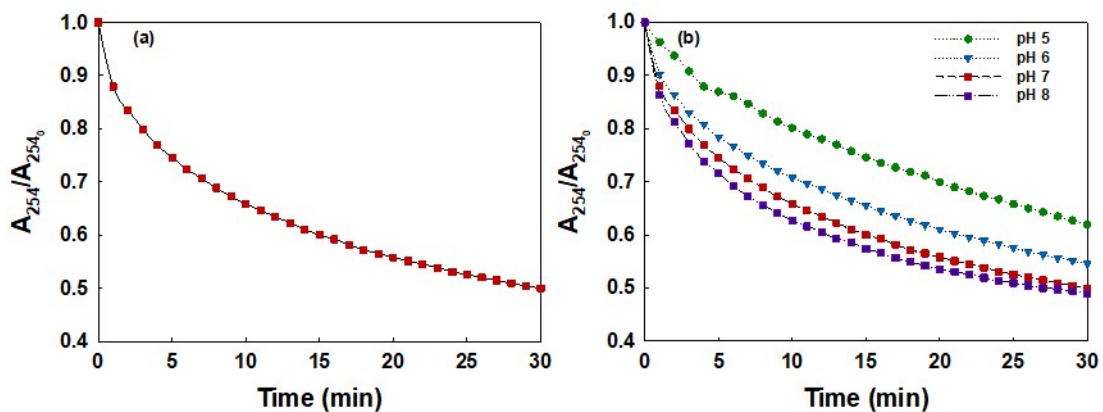
**Fig. S1** (a) Atomic force microscopy (AFM) image of pristine GO. (b) The thickness of GO determined by AFM.



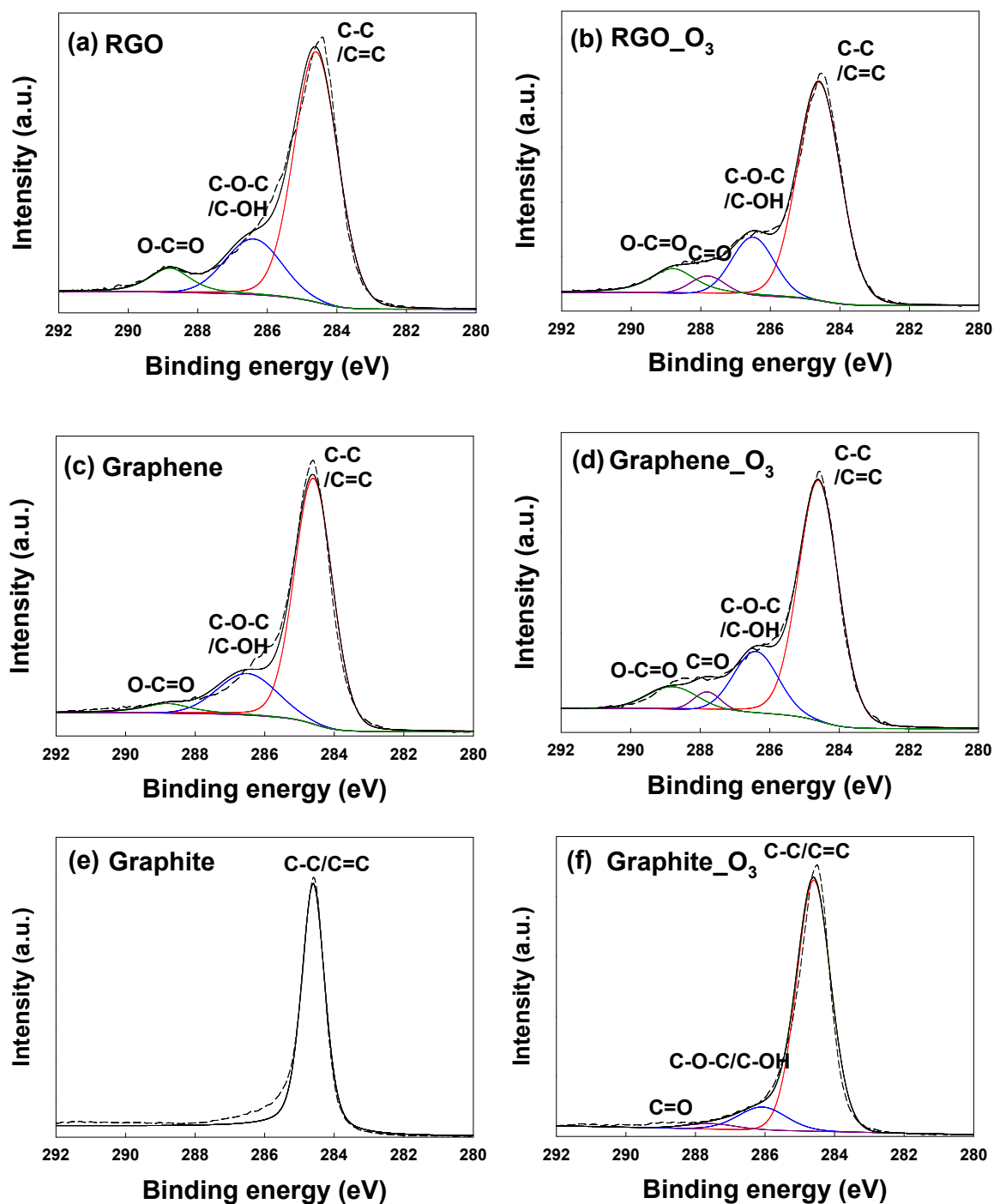
**Fig. S2.** MS spectra of (a) GO and (b) GO<sub>2</sub> acquired from  $m/z$  100-1000 in positive ion mode and shown on the same scale.



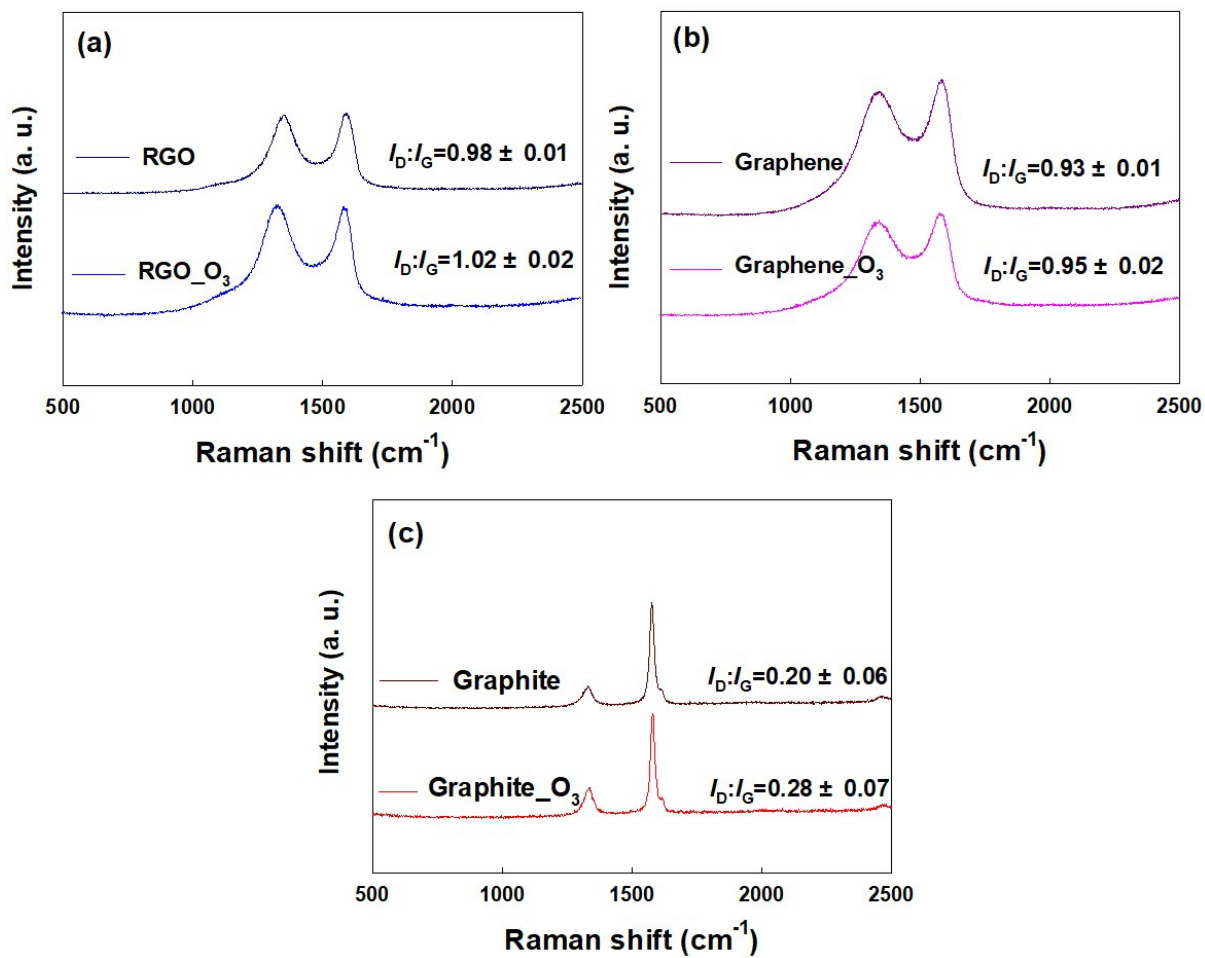
**Fig. S3** SUVA<sub>254</sub> of graphene oxide treated with different dosage of ozone.



**Fig. S4** (a) The oxidation kinetics of GO by ozonation reflected in the change of absorbance at 254 nm (pH = 7). (b) Effect of different pH levels on the oxidation kinetics of GO by ozonation (pH = 5, 6, 7, 8).

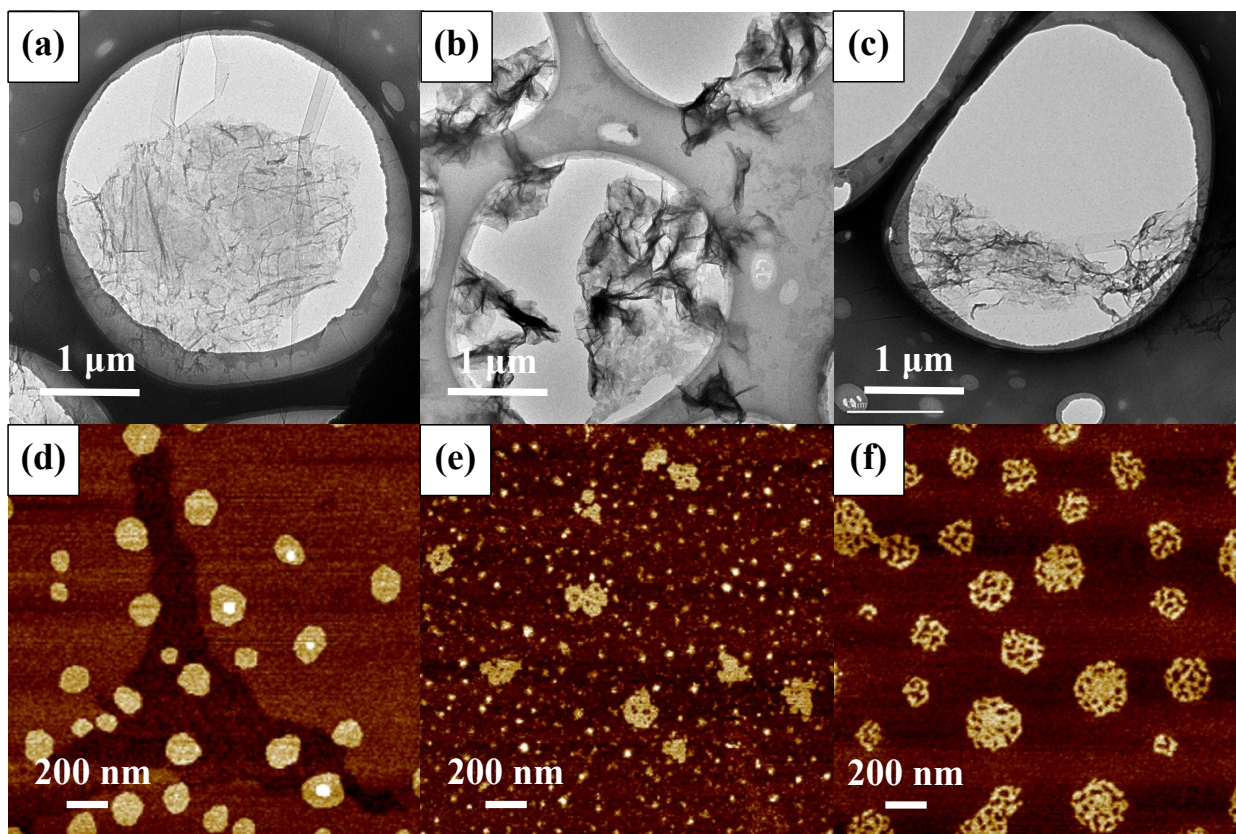


**Fig. S5** X-ray photoelectron spectroscopy (XPS) of (a) RGO, (b) O<sub>3</sub>-treated RGO (RGO<sub>O<sub>3</sub></sub>), (c) graphene, (d) O<sub>3</sub>-treated graphene (Graphene<sub>O<sub>3</sub></sub>), (e) graphite and (f) O<sub>3</sub>-treated graphite (Graphite<sub>O<sub>3</sub></sub>).



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g. S6 Raman spectra of (a) RGO, (b) graphene, (c) graphite before and after  $O_3$  treatment.



**Fig. S7** TEM images of (a) GO, (b) GO<sub>O<sub>3</sub></sub> and (c) GO<sub>O<sub>3</sub></sub> with t-BuOH. AFM images of (d) GO, (e) GO<sub>O<sub>3</sub></sub> and (f) GO<sub>O<sub>3</sub></sub> with t-BuOH.