Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

The key structural features governing the free radical and catalytic activity of graphite/graphene oxide

Supporting figures

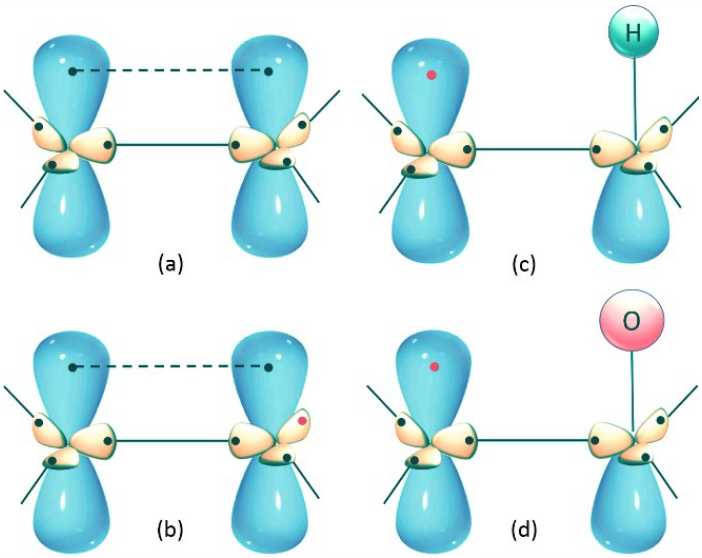


Figure S1. Schematic of half-filled π orbitals with different stability on GO structure when they are located at a) perfect sp^2 domain, b) edges and defect sites where there are missing atoms in the carbon lattice, c) and d) adjacent to the hybridized domains with hydrogen and oxygen atoms, respectively.

Each carbon atom in graphene is covalently bonded through three electrons to three other carbon atoms. The fourth valence electron on each carbon atom form a half-filled orbital which permits free-moving of electrons (Fig. S1 (a)) [1]. These free electrons can form dangling bond states of sigma-electrons at the edge or defect sites of the graphene plane (Fig. S1 (b)). Also, re-hybridization (presence of sp^3 bonds instead of usual sp^2 bonds) cause the formation of dangling bond states of π-electrons (Fig. S1 (c, d)) [2].

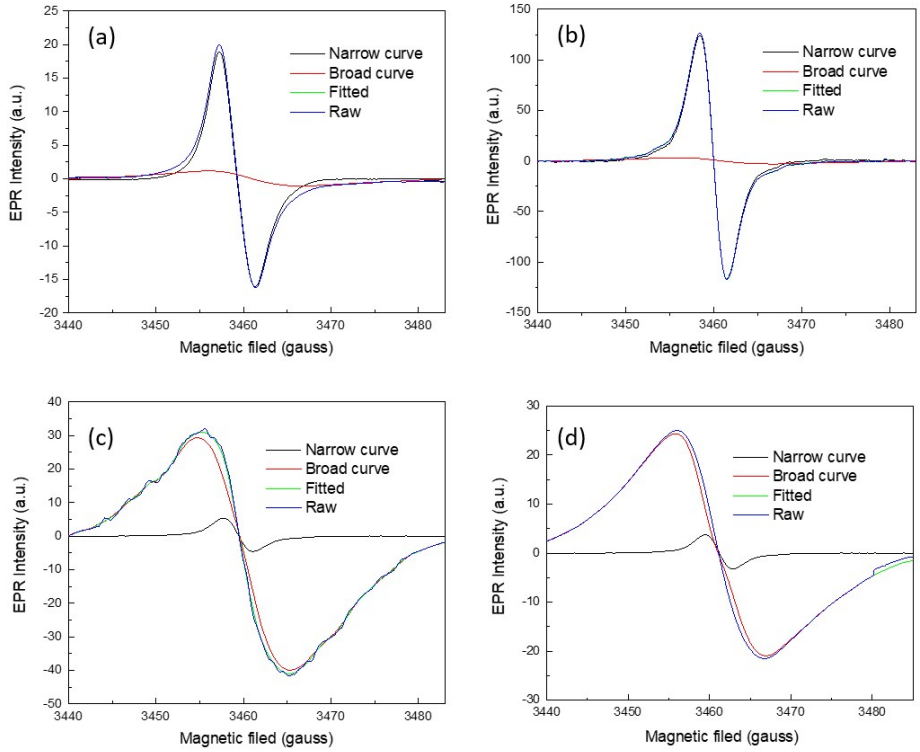


Figure S2. EPR signal and simulation of GO samples a) A, b) F-14h, c) D and d) F-12h.

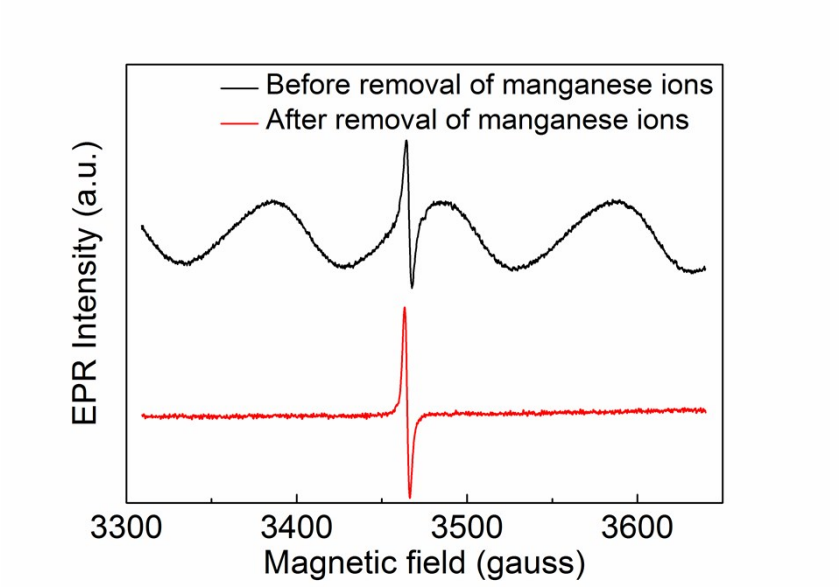


Figure S3. EPR spectra of GO synthesised by the modified Hummer's method before and after removal of Mn^{2+} ions. A hyperfine pattern characteristic of Mn^{2+} ions is shown on GO sample prior to removal of impurities by washing with hydrochloric acid (HCl) and subsequent dialysis.

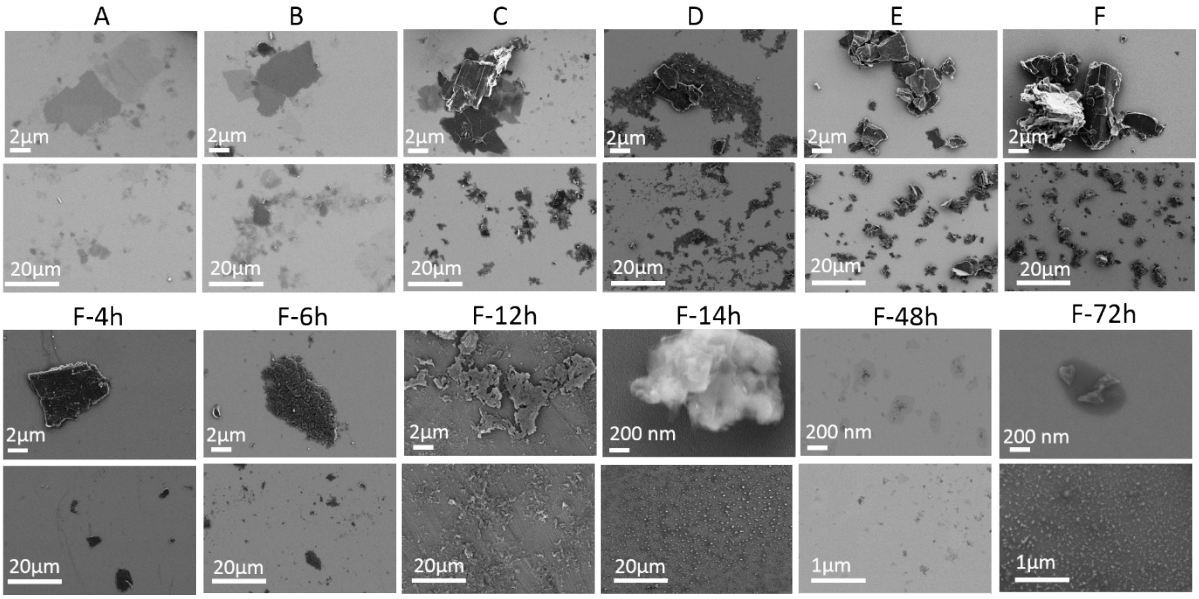


Figure S4. SEM images of GO sheets with two different magnifications. (A-F) obtained with different graphite/$KMnO_4$ ratios (0.25, 0.57, 0.78, 1, 1.43 and 2.8) through the modified Hummer's method and GO sheets obtained after further oxidation (with the mixture of H_2SO_4/HNO_3) of sample F for different durations (4, 6, 12, 14, 48 and 72h).

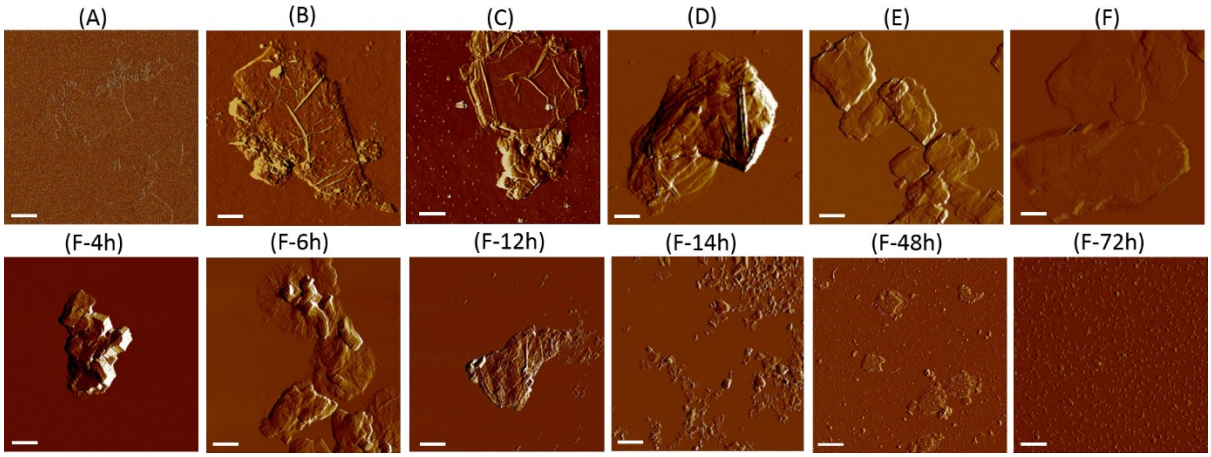


Figure S5. The phase mode images of GO sheets (A-F) obtained with different graphite/$KMnO_4$ ratios (0.25, 0.57, 0.78, 1, 1.43 and 2.8) through modified Hummer's method and GO sheets obtained after further oxidation (with the mixture of H_2SO_4/HNO_3) of sample F for different durations (4, 6, 12, 14, 48 and 72h). The scale bars represent 1 µm.

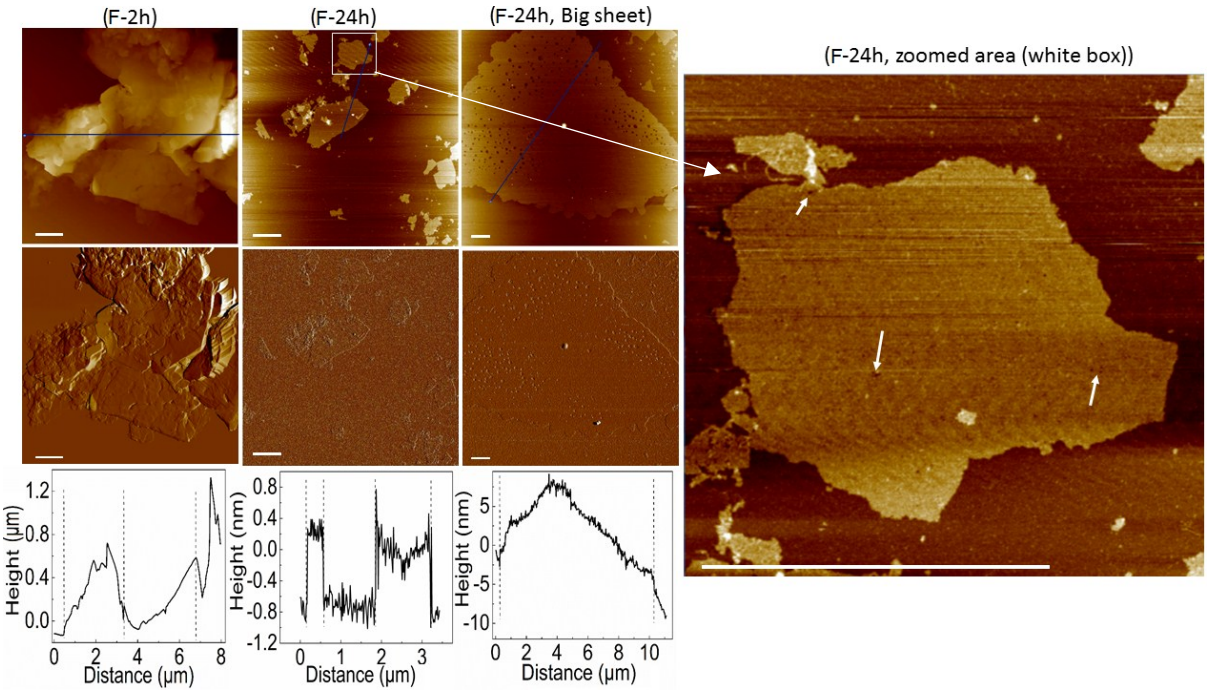


Figure S6. AFM images and thickness distribution of GO sheets obtained after further oxidation (with the mixture of H_2SO_4/HNO_3) of sample F for 2 and 24 h. Some big sheets are detected in sample obtained after oxidation for 24h (F-24h, Big sheets). The holes inside the big sheets are visible while there are some small holes in the small sheets as well (F-24h, zoomed area (white box)). The scale bars represent 1 μm.

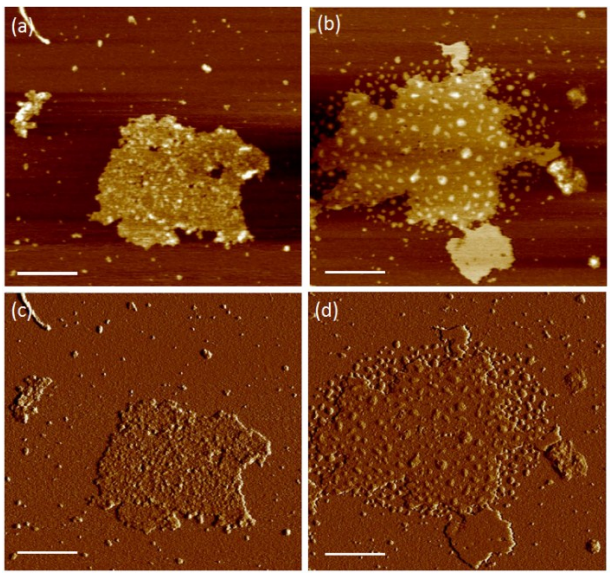


Figure S7. AFM height (a, b) and phase (c, d) images of GO sheets obtained after further oxidation (with the mixture of H_2SO_4/HNO_3) of sample F for 48 h. The scale bars represent 1 μm.

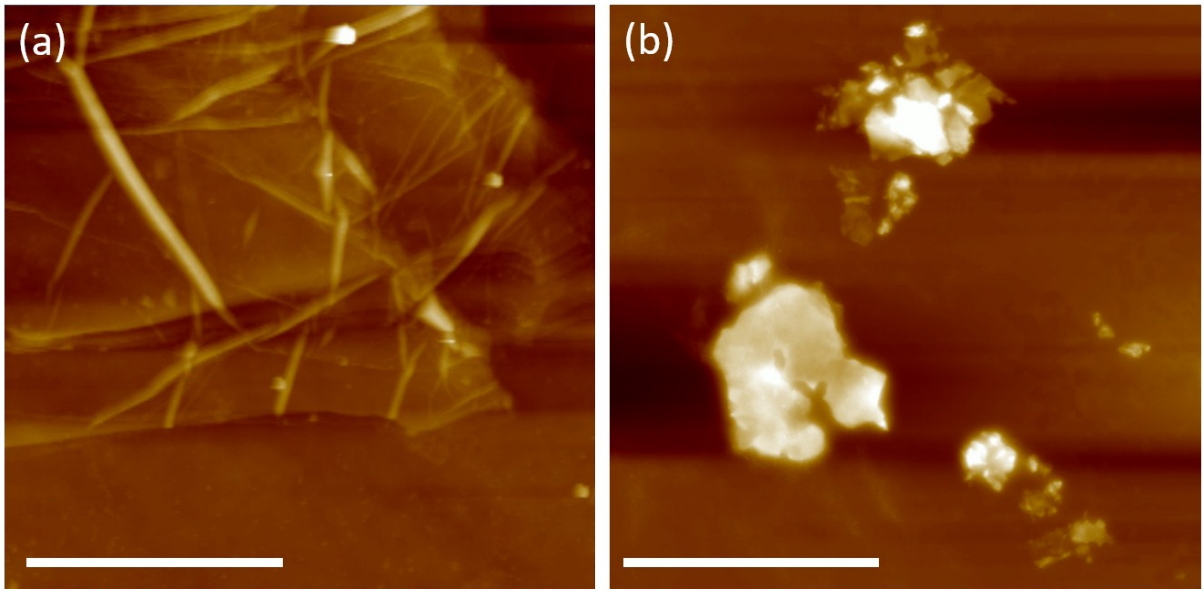
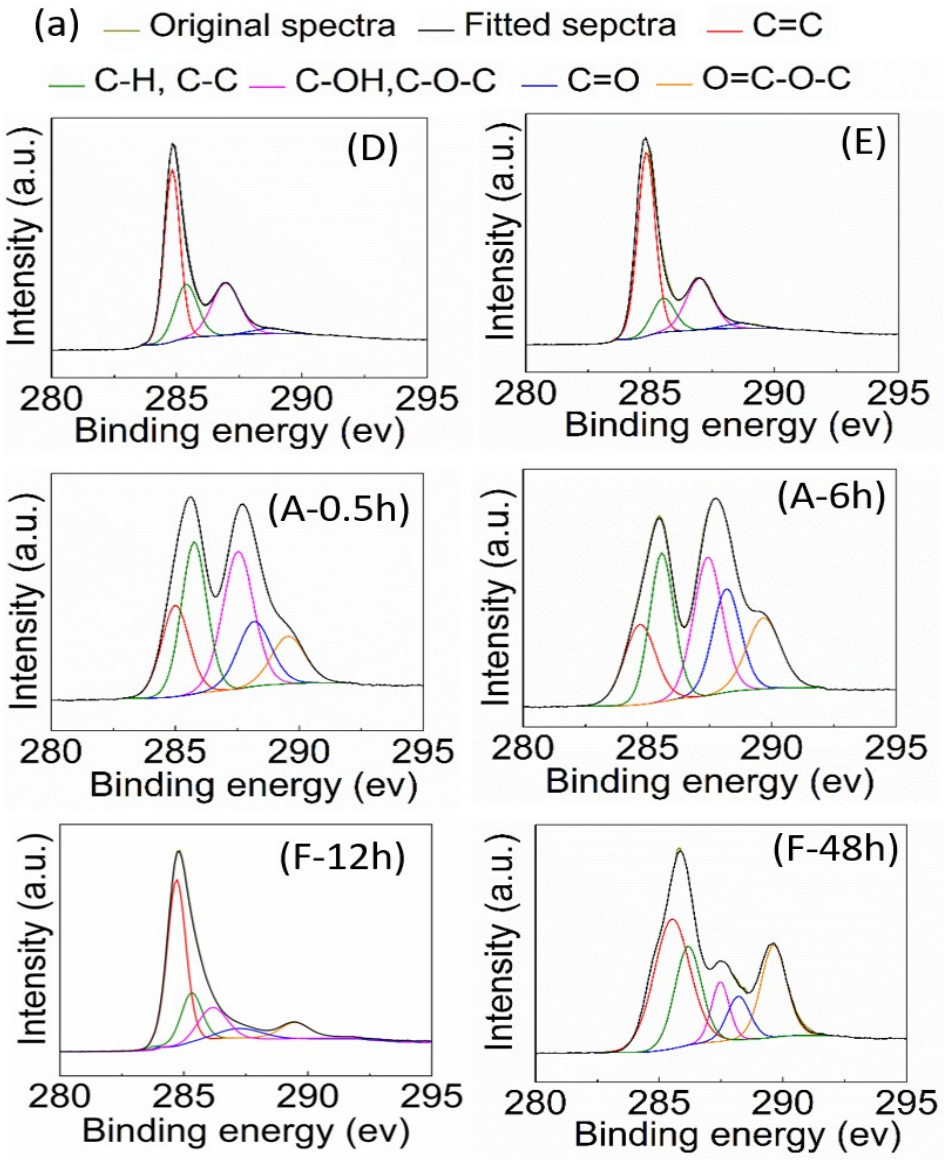


Figure S8. AFM height images of sample C (a) and F-14h (b). The scale bars represent 1 μm.



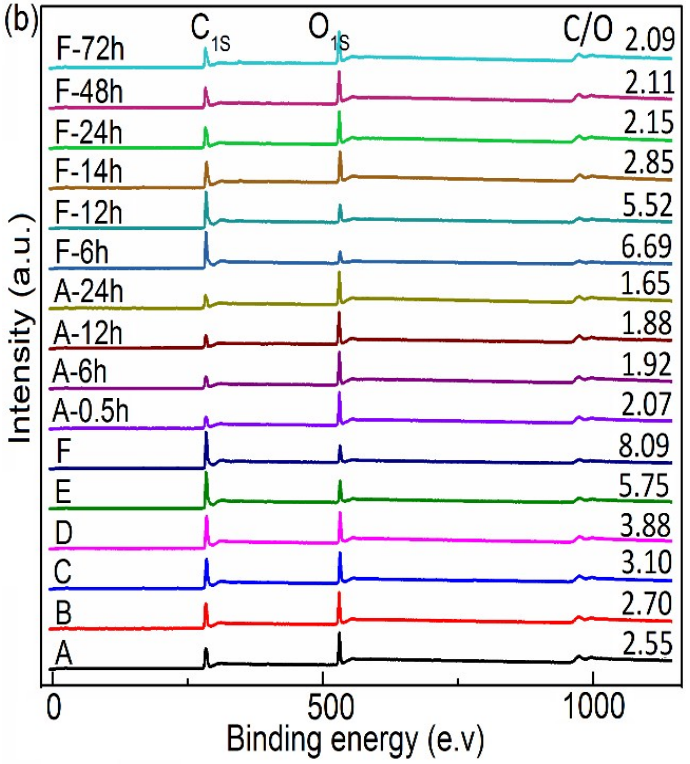


Figure S9. XPS analysis. (a) C1s and (b) survey spectra for GO sheets obtained with different oxidation degrees.

Table S1. Relative percentage of bounds in the C 1s peaks of the XPS data.

Samples	C=C (%)	C-C, C-H (%)	C-O-C, C-OH (%)	C=O (%)	O=C-O-C (%)	C/O ratio
A	39	3	52	6	0	2.55
B	42	4	47	7	0	2.70
C	45	17	32	6	0	3.10
D	52	11	30	5	0	3.88
E	58	14	25	3	0	5.75
F	69	10	19	2	0	8.09
A oxidized 0.5h in acid (A-0.5h)	17	25	30	16	12	2.07
A oxidized 6h in acid (A-6h)	16	25	25	19	15	1.92
A oxidized 12h in acid (A-12h)	14	24	27	21	14	1.88
A oxidized 24h in acid (A-24h)	12	20	32	18	18	1.65
F oxidized 6h in acid (F-6h)	55	13	19	9	4	6.69
F oxidized 12h in acid (F-12h)	50	15	17	10	7	5.52
F oxidized 14h in acid (F-14h)	44	16	23	10	8	2.85
F oxidized 48h in acid (F-48h)	37	20	11	11	21	2.11
F oxidized 72h in acid (F-72h)	35	19	11	10	25	2.09

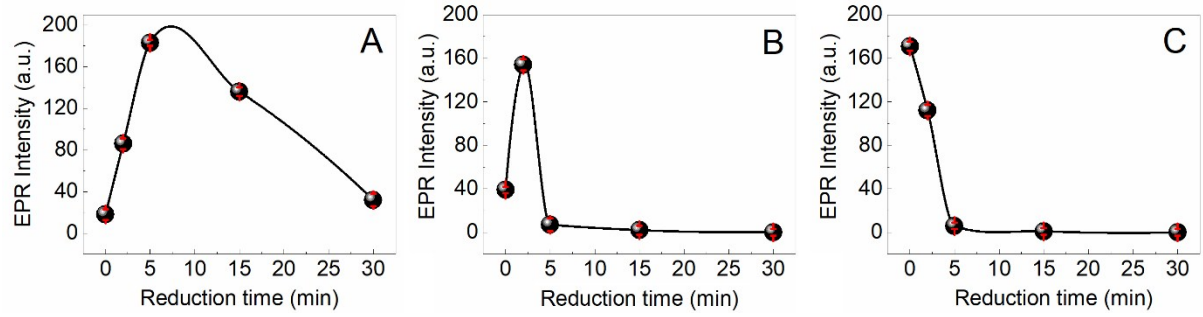


Figure S10. Changes in the EPR intensities of samples A-C as a function of reduction (thermal reduction at 170 ºC) time.

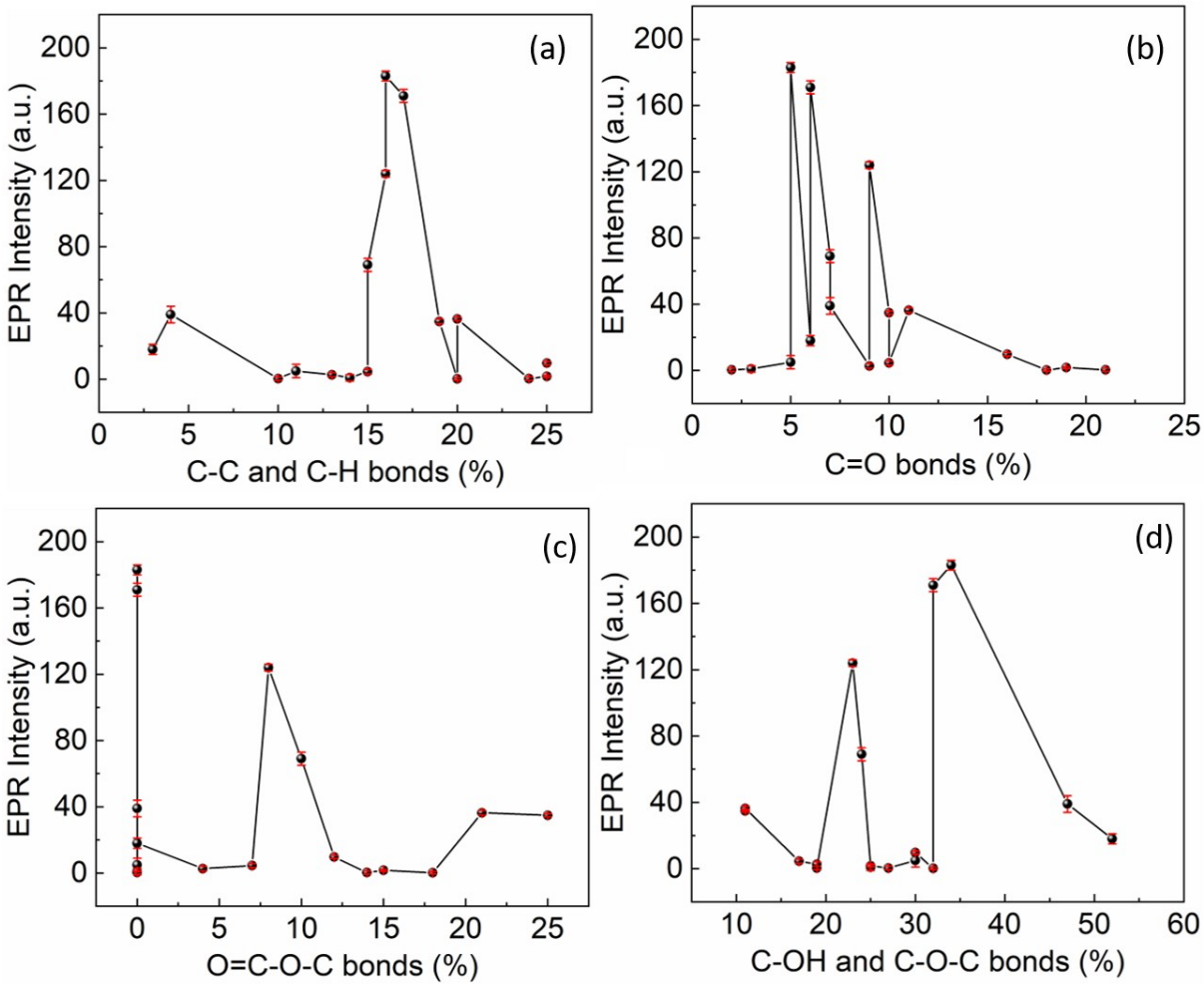


Figure S11. EPR intensity of GO as a function of (a) C-C, C-H bond fraction (b) C=O bond fraction, (c O=C-O-C bond fraction and (d) C-OH, C-O-C bond fraction.

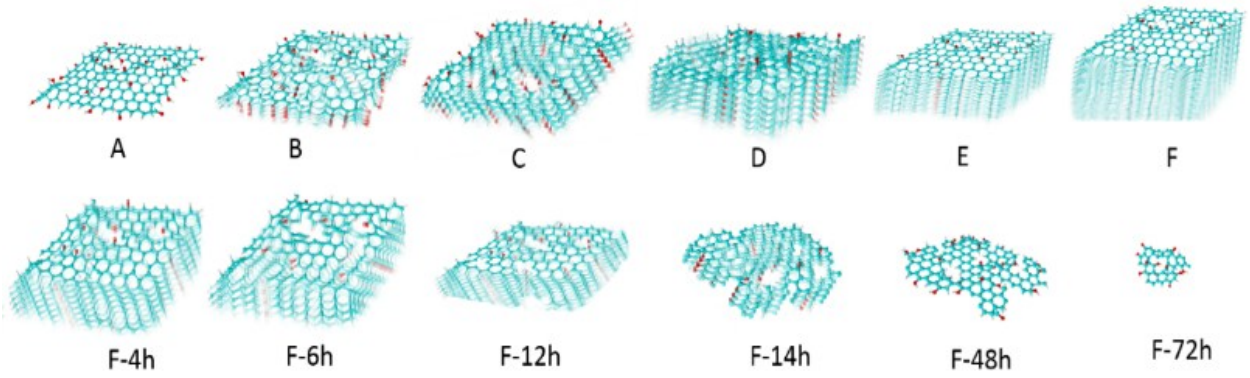
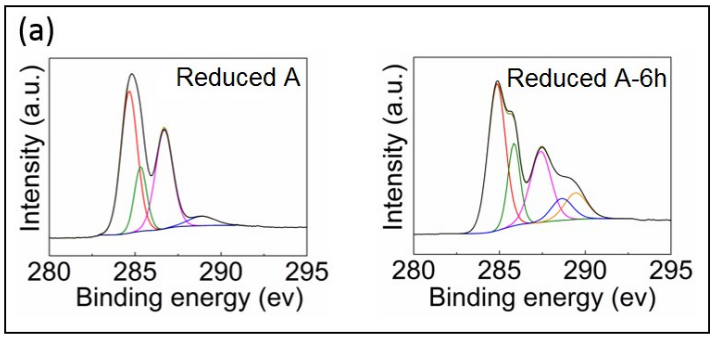


Figure S12. Schematic of the physical and chemical features of GO sheets (A-F) obtained with different graphite/$KMnO_4$ ratios (0.25, 0.57, 0.78, 1, 1.43 and 2.8) and GO sheets obtained at the ratio of 2.8 (Sample F) after being oxidized with acids for different durations (4-72h).



(b)

Samples	C=C (%)	C-C, C-H (%)	C-O-C, C-OH (%)	C=O (%)	O=C-O-C (%)	C/O ratio
Reduced A	46	15	34	5	0	3.02
Reduced A-6h	43	16	24	7	10	2.78

Figure S13. The XPS analysis, (a) C1s and (b) relative percentage of bonds in the C 1s peaks for two different GO (reduced A and reduced A-6h) sheets after thermal reduction at 170 ºC for 5 minutes. The EPR intensities of Reduced A and Reduced A-6h are 188 and 73, respectively.

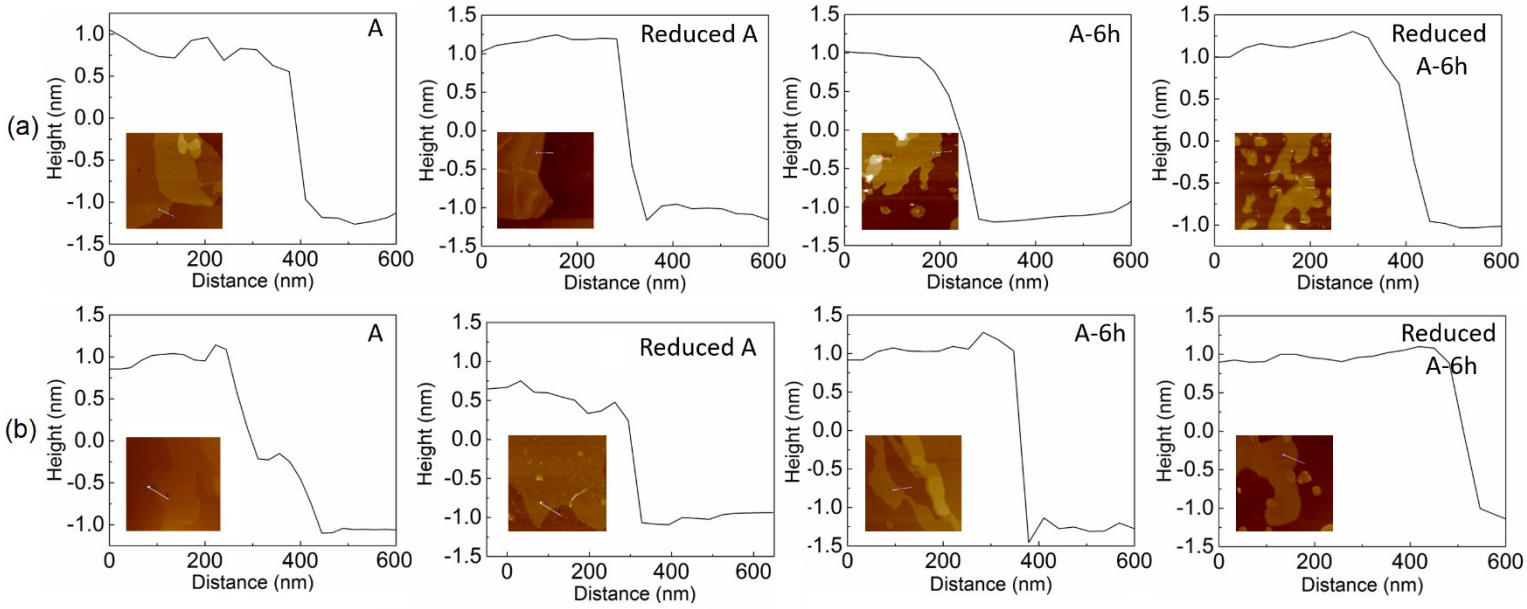


Figure S14. Thickness distribution of GO sheets. (a) Samples used for EFM characterizations and (b) sample used for MFM characterizations.

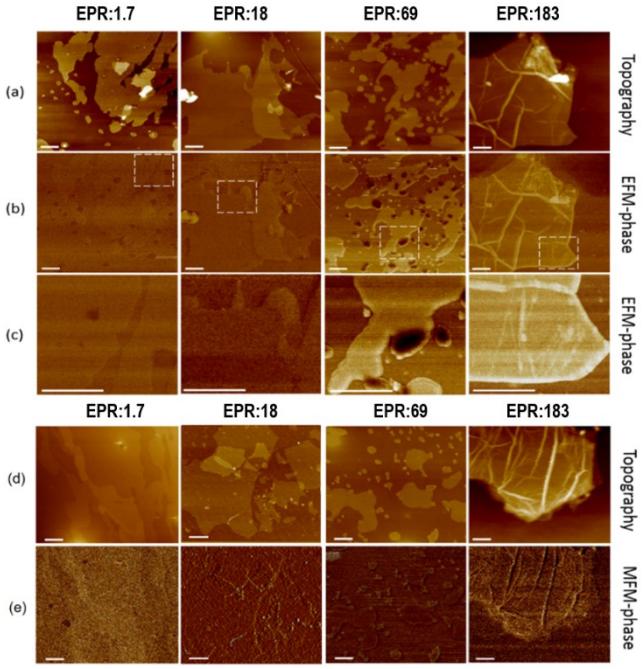


Figure S15. Surface electronic and magnetic properties of GO sheets with different radical contents. (a) Topography and (b) EFM-phase images of different GO samples on silicon wafer substrate, with V_{tip} = +2 V (z = 20 nm) (c) Higher resolution EFM images of the square areas in (b), (d) Topography and (e) MFM-phase images of different GO samples (z = 20 nm). The scale bars represent 1 μm.

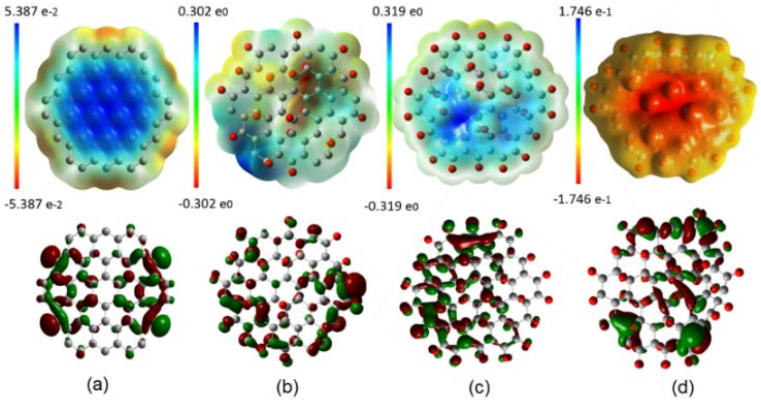


Figure S16. Electrostatic potential mapping from charge density matrix for different samples including: a) pristine graphene, b) partially oxidized GO, c) highly oxidized GO, and d) over oxidized GO.

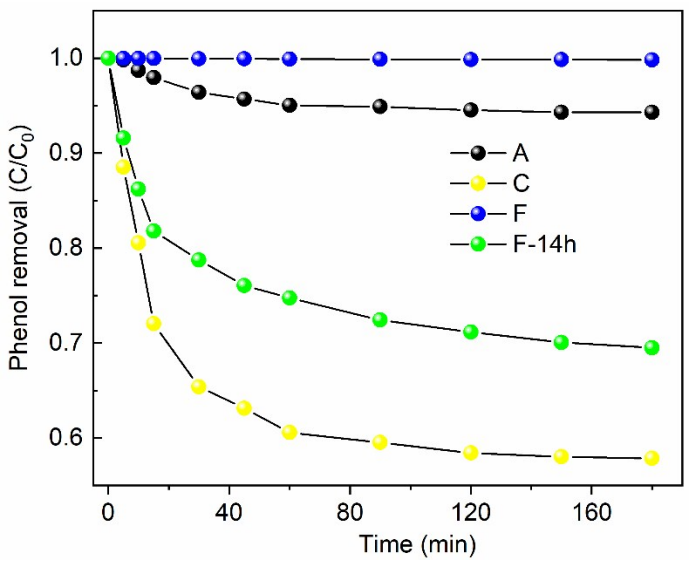


Figure S17. The phenol removal efficiencies of various graphite oxide/GO samples in the absence of PMS.

References

1. N. Peres, *Europhys. News*, 2009, **40**, 17-20.

2. T. Alonso-Lanza, F. Aguilera-Granja, J. González and A. Ayuela, *Phys. Rev. Mater.*, 2017, **1**, 024001.