Supporting Information

Underlying Mechanisms of Reactive Oxygen Species and Oxidative Stress photoinduced by Graphene and its Surface Functionalized Derivatives

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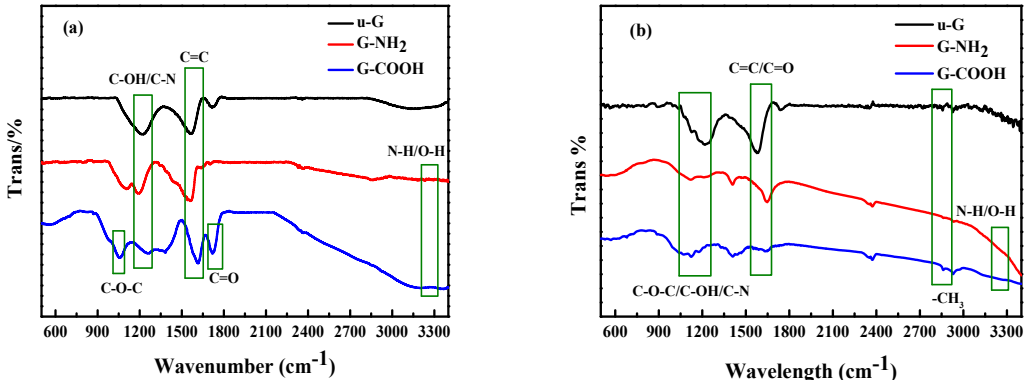


Figure S1. Fourier transform infrared spectra of G-COOH, G-NH_2 and u-G before (a) and after 5 h (b) irradiation treatments.

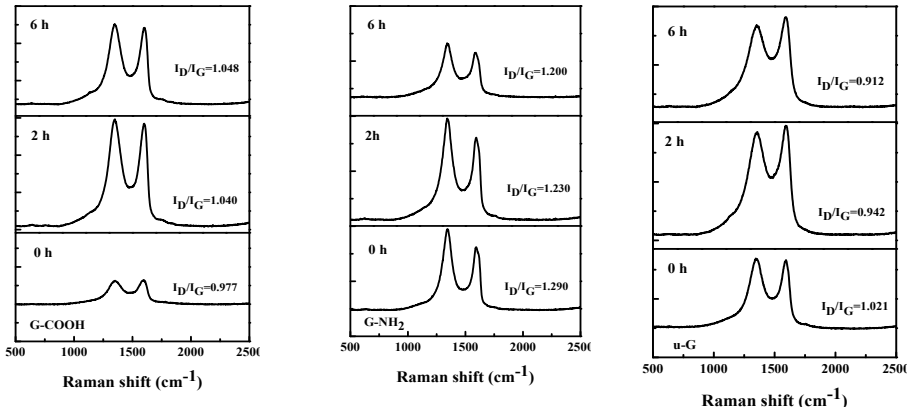


Figure S2. The Raman spectrum of G-COOH, G-NH_2 and u-G before and after 2 h and 6 h irradiation.

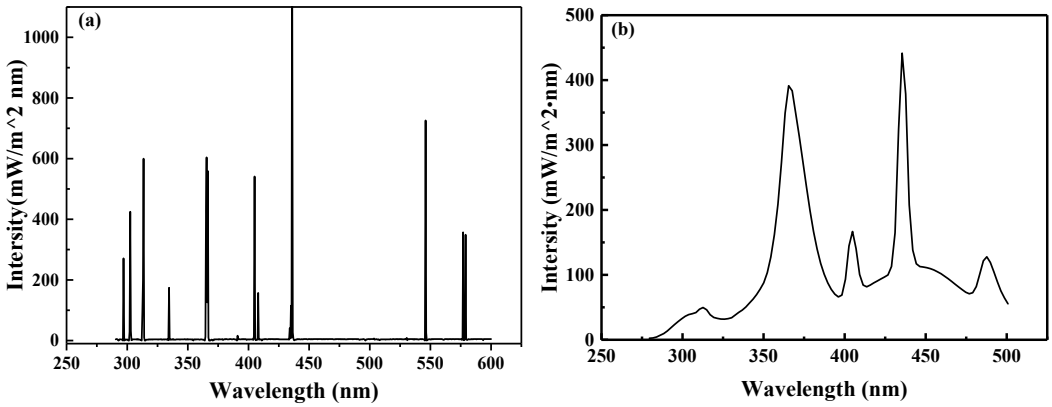


Figure S3. Spectrum of radiation for experiment. (a) Spectrum of mercury lamp; (b) Spectrum of simulated sunlight radiation

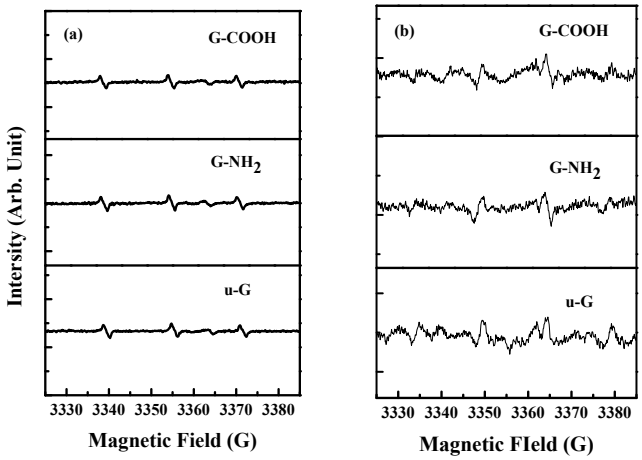
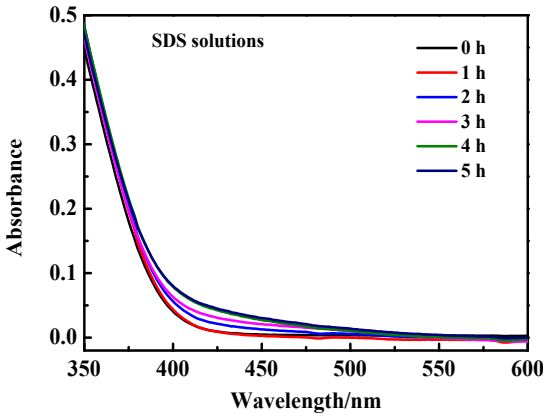


Figure S4. EPR spectrum recorded at ambient temperature for (a) TEMP adduct with $^1O_2$ and (b) DMPO adduct with •OH in G-COOH, G-NH_2 and u-G suspensions in the dark (graphene of 15 mgC/L).



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48 **Figure S5.** Absorbance of XTT formation indicating $O_2^{\bullet-}$ production in SDS solutions by XTT

49 (0.1 mM) under lamps light.

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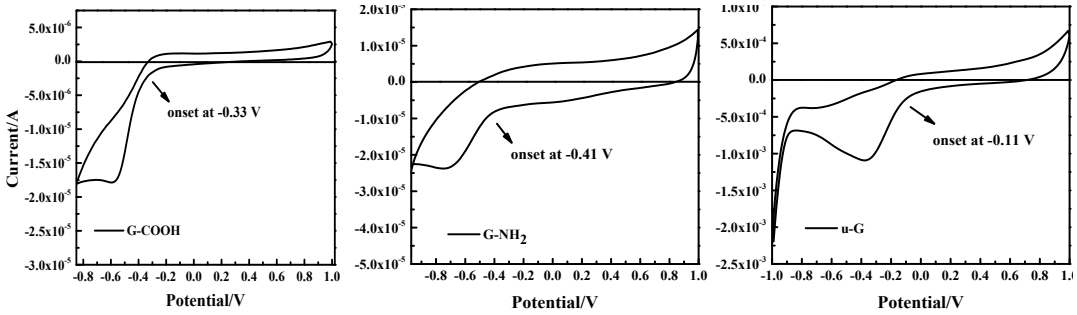


Figure S6. Cyclic voltammetry curves of G-COOH, G-NH_2 and u-G on a Pt/C substrate at a sweep rate of 50 mV/s.

The electrochemical properties of G-COOH, G-NH_2 and u-G were investigated by cyclic voltammetry. As shown in the cyclic voltammetry curves, G-COOH, G-NH_2 and u-G have one irreversible reduction, but no oxidation. The E_{HOMO} and E_{LUMO} (relative to the vacuum level) can be calculated by using the electrochemical method with the following equation:[1-2]

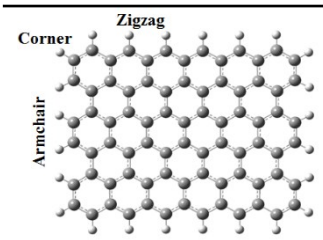
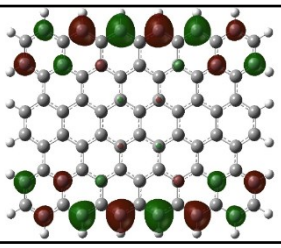
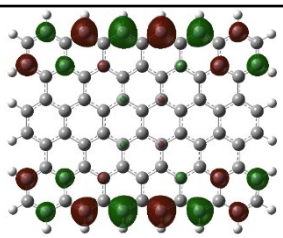
$$E_{LUMO} \text{ (or } E_{HOMO}) = -4.5 - eE^{red}_0 \text{ (or } E^{ox}_0)$$

where, E^{red}_0 and E^{ox}_0 represent reduction and oxidation potentials corresponding to reference electrode, respectively, E_{LUMO} and E_{HOMO} are relative to the absolute vacuum scale (AVS). In this study, E^{red}_0 was determined from the onsets of the reduction peaks.

[1] Cernini R, Li X C, Spencer G W C, et al. Electrochemical and optical studies of PPV derivatives and poly (aromatic oxadiazoles). Synthetic metals, 1997, 84(1): 359-360.

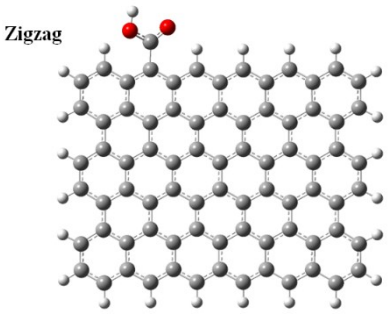
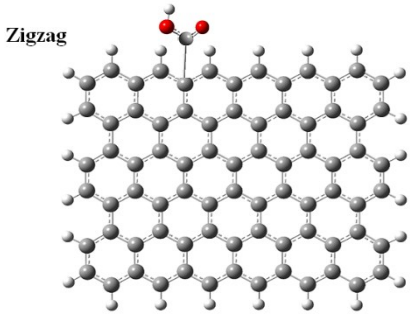
[2] Usta H, Risko C, Wang Z, et al. Design, synthesis, and characterization of ladder-type molecules and polymers. Air-stable, solution-processable n-channel and ambipolar semiconductors for thin-film transistors via experiment and theory. Journal of the American Chemical Society, 2009, 131(15): 5586-5608.

Table S1. Optimized configurations and frontier molecular orbitals energies of u-G.

		
configuration	E_{LUMO}= -3.84 eV	E_{HOMO}= -4.09 eV

* Active site of u-G was at the edges of graphene sheet.

Table S2. Description on substitution sites of functionalized graphene.

	α-site	β-site
configuration		

* There are two kinds of substitution sites at the zigzag edges: α-site (left) and β-site (right).[3] The energy for β-site are lower that α-site at the zigzag edges.

[3] Kobayashi Y, Fukui K, Enoki T, et al. Edge state on hydrogen-terminated graphite edges investigated by scanning tunneling microscopy. Physical Review B, 2006, 73(12): 125415-125423.

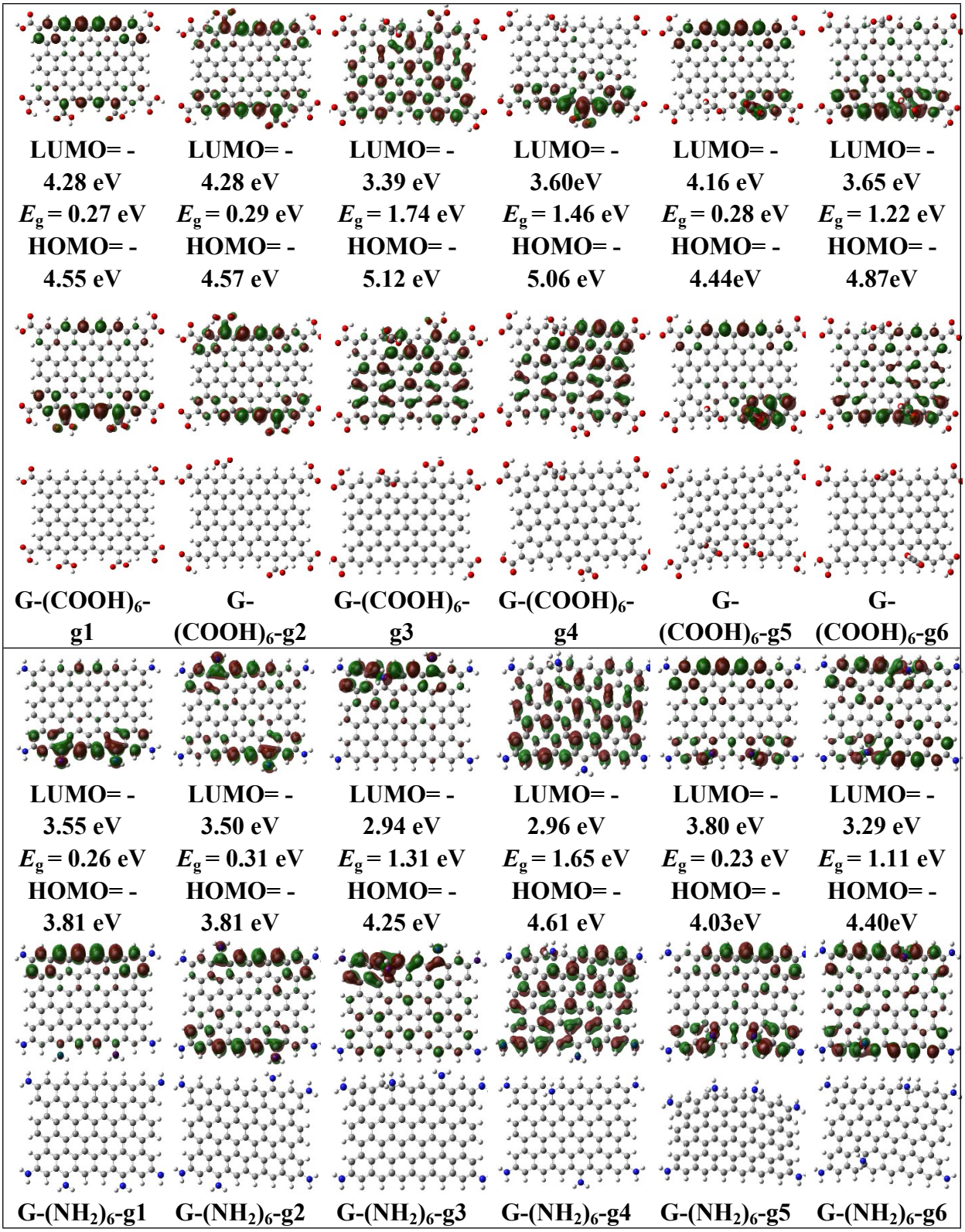
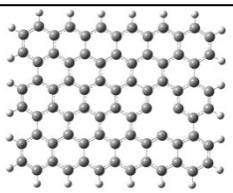
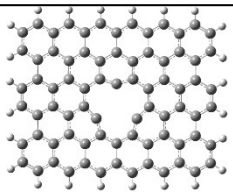
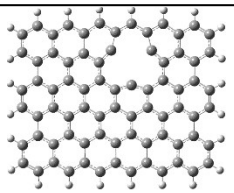
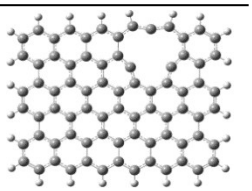


Figure S7. Optimized configurations and frontier molecular orbitals energies of G-COOH and G-NH_2. The possible 6 configurations with 6 functional groups were considered in the calculation of E_{HOMO} and E_{LUMO} for G-COOH and G-NH_2. In this calculation, 4 carboxyl groups were added to the corner sites of graphene sheet and the remaining 2 carboxyl groups were added to the α-site or β-site of the zigzag edge. Amino group was also considered to have similar substitution mode with carboxyl group.

Table S3. The configurations and frontier molecular orbitals energies of u-G with defect*.

	G-defect-g1	G-defect-g2	G-defect-g3	G-defect-g4
configuration				
E_{LUMO} (eV)	-3.844	-3.888	-3.770	-4.098
E_{HOMO} (eV)	-4.099	-4.144	-4.050	-4.368
E_g(eV)	0.255	0.256	0.280	0.270

*G-defect-g1 indicates that graphene with defect is on the center of graphene sheet, and G-defect-g2 indicates that graphene with defect is close to the zigzag edge.