Supplementary Information

How Fast is the Reaction of Hydrated Electrons with Graphene Oxide in Aqueous Dispersions?

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Transient absorption spectra of solvated electron + ai-GO, absorption time profiles and pseudo-first-order fits for determination of rate constants.

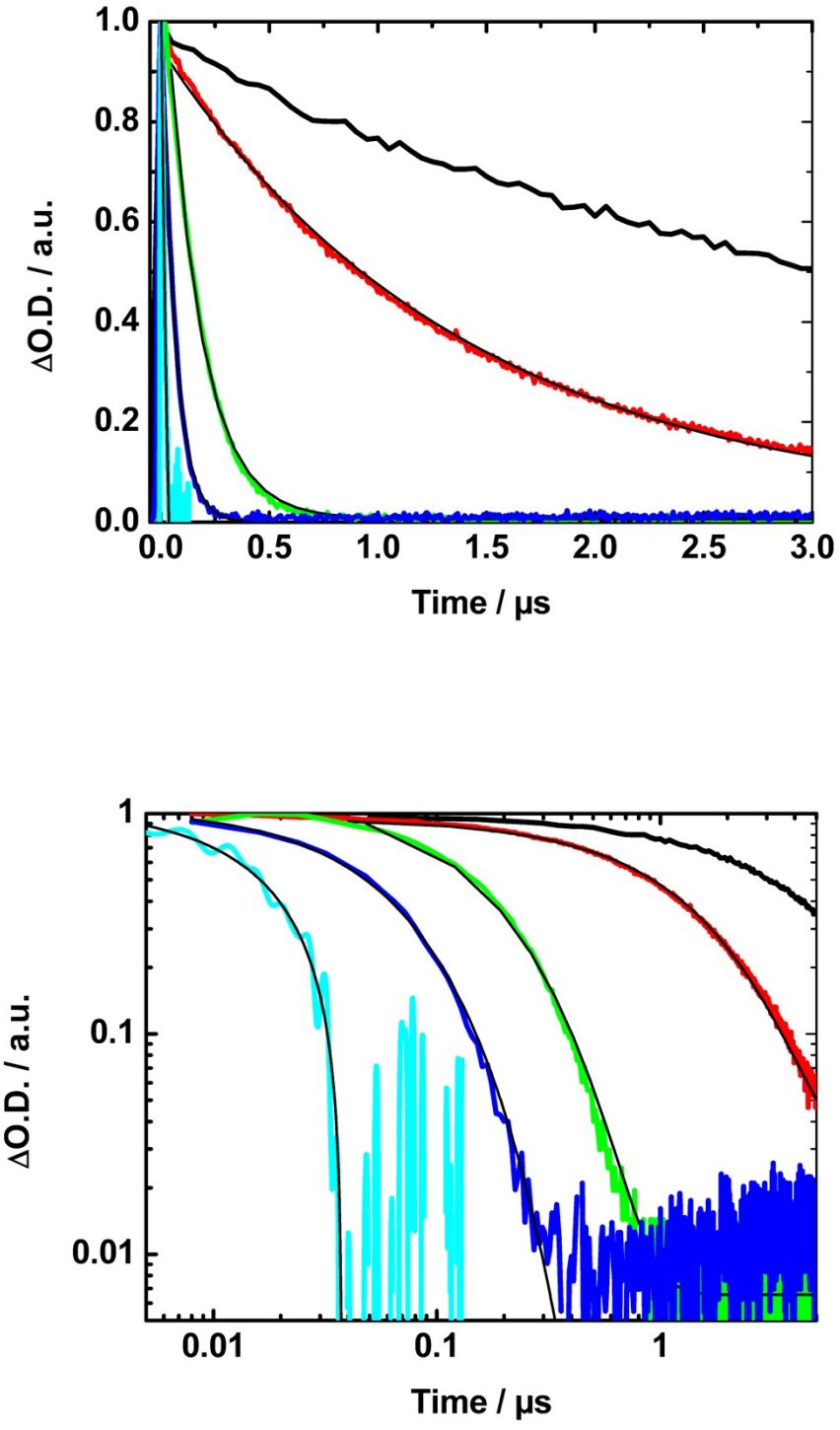

Figure S1: Fits (pseudo first order) of the traces in Fig. 1b.

Transient absorption spectra of solvated electron + CT-GO, absorption time profiles and plot of the pseudo-first-order rate constant vs. the CT-GO concentration.

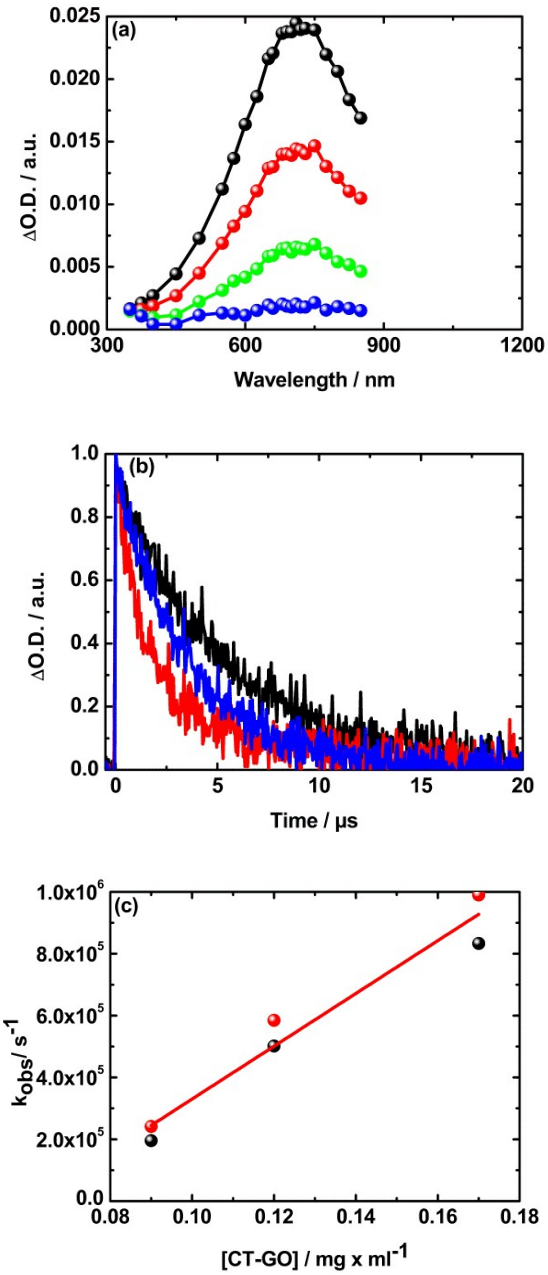

Figure S2. (a): Differential absorption spectra obtained upon electron pulse radiolysis (5 Gy, 15 ns FWHM) of 0.12 mg × ml^{-1} CT-GO in N_2-saturated aqueous solution in the presence of 5 vol.% *t*-butanol with time delays of 80 ns (black), 2 µs (red), 5 µs (green) and 10 µs (blue) after the electron pulse. (b): Absorption time profiles upon electron pulse radiolysis (2.3 Gy, 15 ns FWHM) at 720 nm for solutions 0.09 mg × ml^{-1} CT-GO (red curve), 0.12 mg × ml^{-1} CT-GO (green curve) and 0.17 mg × ml^{-1} ai-GO (blue curve). (c): Plot of the pseudo-first-order rate constants vs. the CT-GO concentration for the decay of the hydrated electrons measured at 720 nm. The red points were obtained with a dose of 5 Gy and the black points with 2.3 Gy.

Transient absorption spectra of solvated electron + NI-GO, absorption time profiles and plot of the pseudo-first-order rate constant vs. the NI-GO concentration.

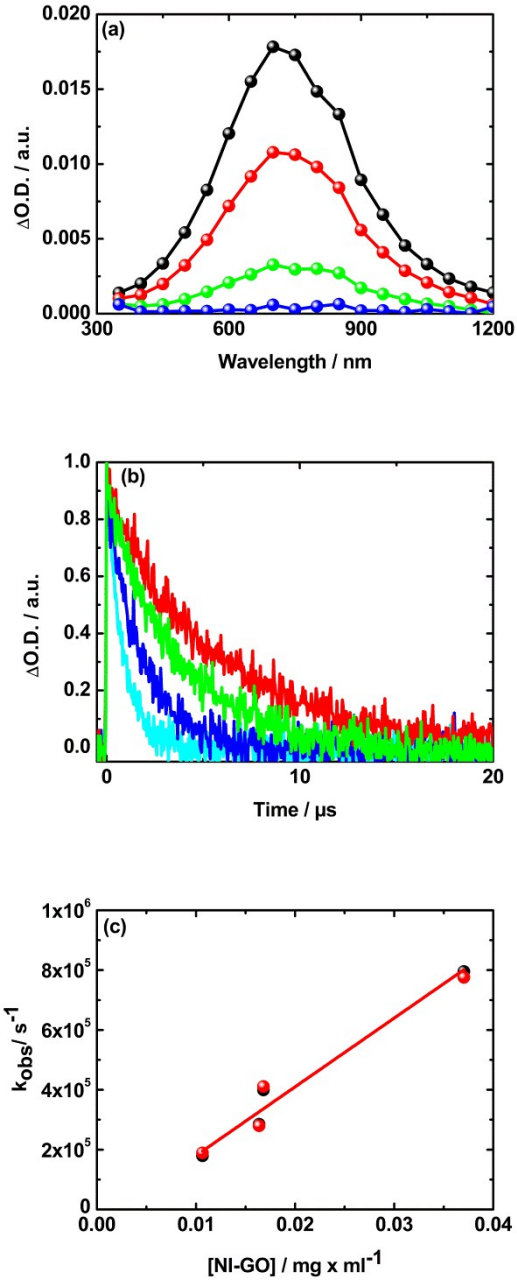

Figure S3. (a): Differential absorption spectra obtained upon electron pulse radiolysis (5 Gy, 15 ns FWHM) of 0.016 mg × ml^{-1} NI-GO in N_2-saturated aqueous solution in the presence of 5 vol.% *t*-butanol with time delays of 80 ns (black), 2 µs (red), 5 µs (green) and 10 µs (blue) after the electron pulse. (b): corresponding absorption time profiles at 720 nm for solutions 0.011 mg × ml^{-1} NI-GO (red curve), 0.016 mg × ml^{-1} NI-GO (green curve), 0.017 mg × ml^{-1} NI-GO (blue curve) and 0.037 mg × ml^{-1} NI-GO (cyan curve) upon pulse radiolysis (2.3 Gy, 15 ns FWHM). (c): Plot of the pseudo-first-order rate constants vs. the NI-GO concentration for the decay of the hydrated electrons measured at 720 nm. The red points were obtained with a dose of 5 Gy and the black points with 2.3 Gy.

Comparison between a simulated absorption time profiles and the measured one.

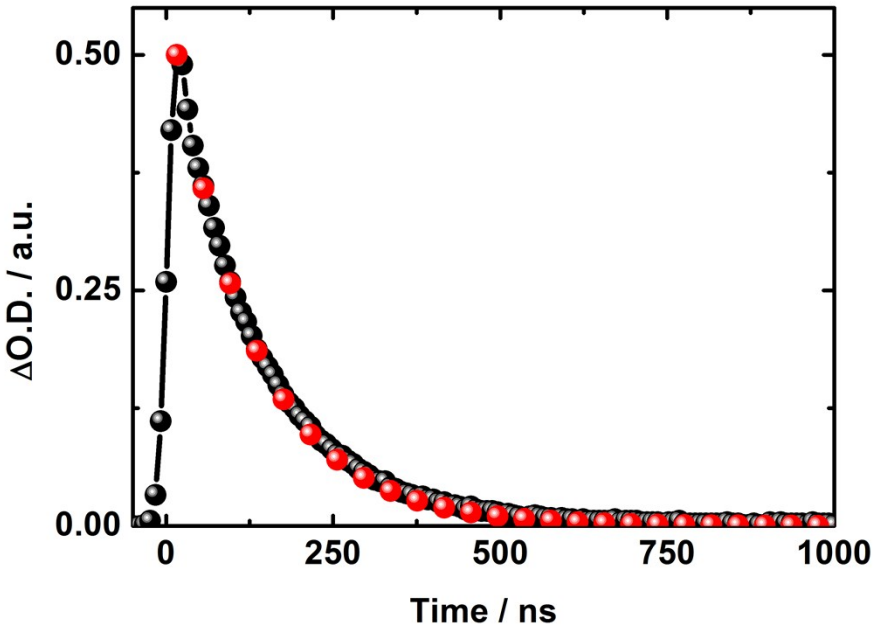

Figure S4. Example of an absorption time profile (black) at 720 nm of ai-GO (0.31 mg x ml^{-1}) upon pulse radiolysis (100 Gy, 15 ns FWHM) in N_2 saturated aqueous solution in the presence of 5 vol% *t*-BuOH and corresponding kinetic simulations of the absorption time profiles (red) for $e_{(aq)}$ using ACCUCHEM[1] with the rate constants stated below. The rate constants for the recombination of $e_{(aq)}^-$ and the reaction of $e_{(aq)}^-$ with H^+ were taken from the literature.[2]

$e_{(aq)}^- + GO \rightarrow rGO$ $\quad k_2 = 2.65 \times 10^7$ ml x mg^{-1} x s^{-1} (1)

$e_{(aq)}^- + e_{(aq)}^- + 2\ H_2O \rightarrow H_2 + {}_2OH^-$ $\quad 2k = 1.1 \times 10^{10}\ M^{-1}s^{-1}$ (2)

$e_{(aq)}^- + H^+ \rightarrow {}^{\bullet}H$ $\quad k_2 = 2.3 \times 10^{10}\ M^{-1}s^{-1}$ (3)

Absorption spectrum of ai-GO dispersed in water.

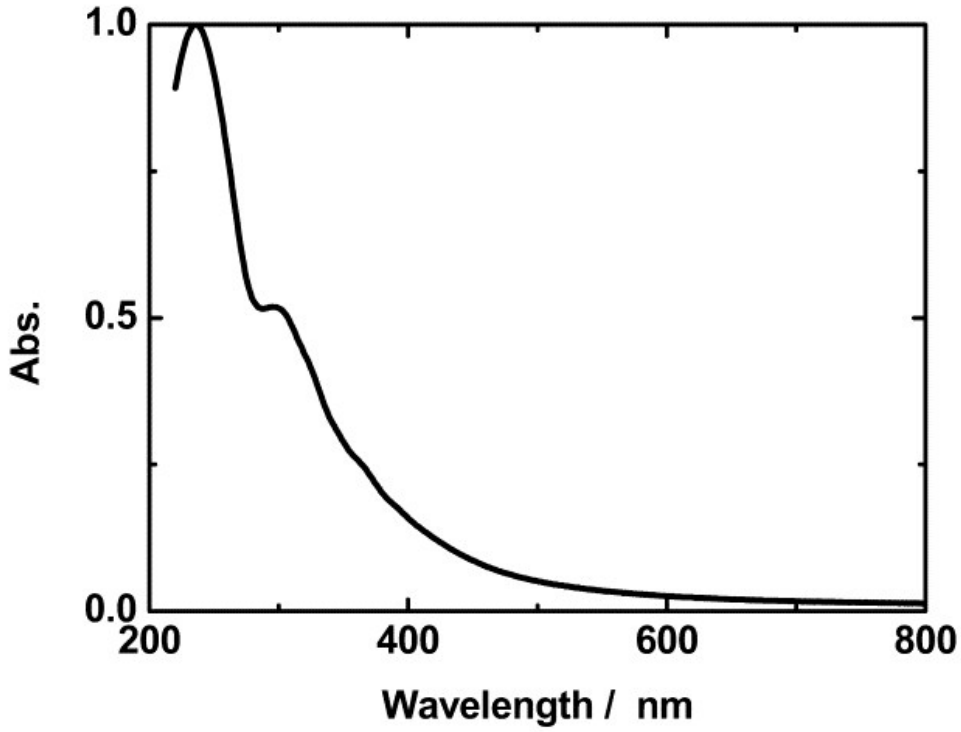

Figure S5. Absorption spectrum of ai-GO dispersed in water.

Transient absorption spectra, time profiles and energy variation of CT-GO upon fs-laserphotolysis

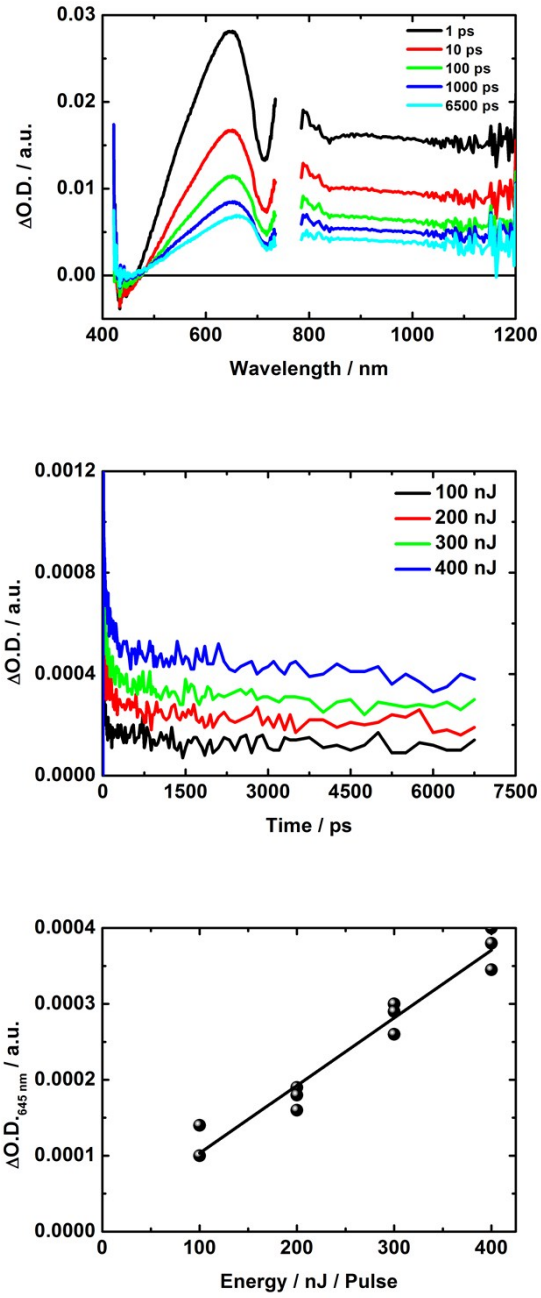

Figure S6. Upper part: Transient absorption spectra of CT-GO (0.2 mg / ml) in water upon fs-laser photolysis (256 nm / 400 nJ) with several time delays. Middle part: Corresponding time absorption profiles at 645 nm at different excitation energies ranging from 100 to 400 nJ / pulse) Lower part: Plot of the transient absorption obtained for the time delays 6250, 6500 and 6750 ps vs. the excitation energy. The black line represents the linear fit.

Possible reaction pathways induced by excitation (266nm) of GO with $COO^{(-)}$ or COOH.

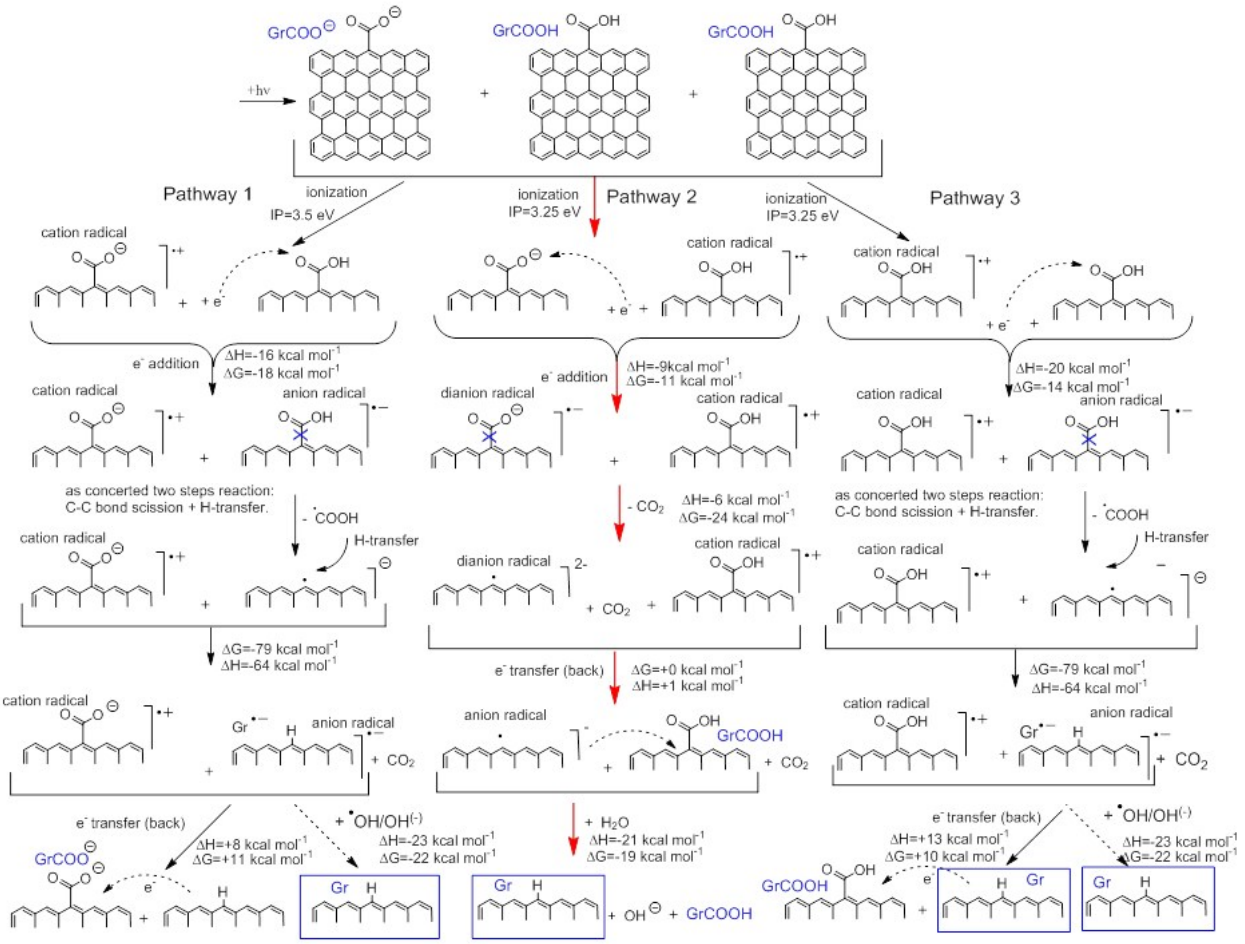

Figure S7. The possible reaction pathways induced by excitation (266nm) of GO with $COO^{(-)}$ or COOH connected to the zig-zag edges of graphene sheet, which could lead to reduced graphene oxide (rGO). Though all three pathways are energetically possible, the pathway 2 seems to be most probable, because the OH radical is not involved. It should be noted, that the concerted two step reaction, namely C-C bond scission with simultaneous H-shift, could proceed with very low activation energy due to assistance of explicit water molecule.

Frontier molecular orbitals of model structure of GrO with COOH group connected to the zig-zag edges.

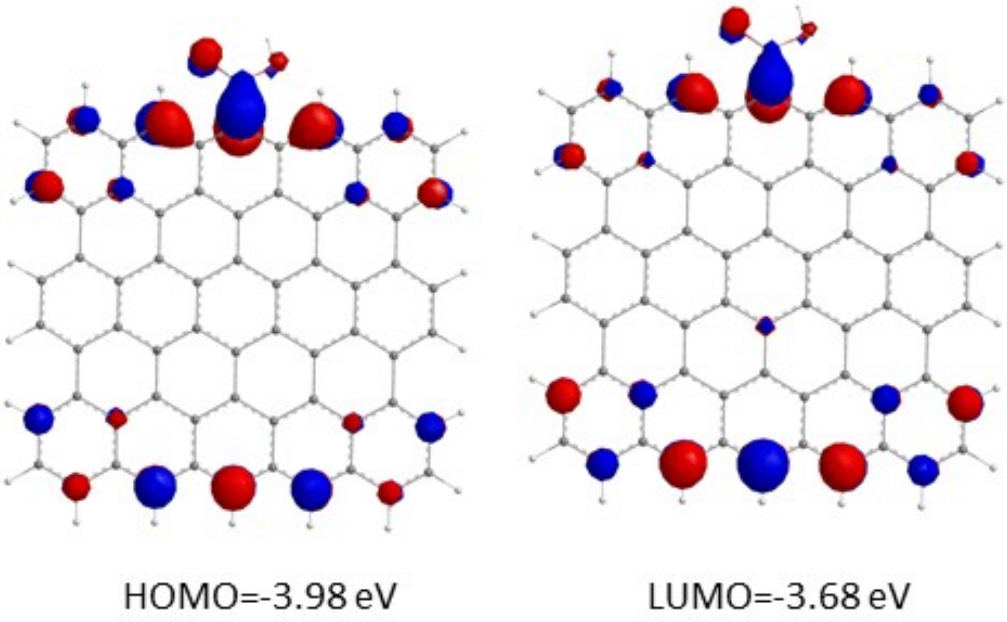

Figure S8. Frontier molecular orbitals (Isocontour 0.035) of model structure of GO with COOH group connected to the zig-zag edges. As can be seen the strongest localization of both HOMO and LUMO is calculated on the COOH defect of graphene sheet indicating the most reactive place in molecule.

References

1 W. Braun, J. T. Herron and D. K. Kahaner, *Int. J. Chem. Kinet.,* 1988, 20, 51.
2 K. P. Madden and S. P. Mezyk, *J. Phys. Chem. Ref. Data* 2011, 40, 023103-1.