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# Associative behavior and role of functional groups on the fluorescence of graphene oxide

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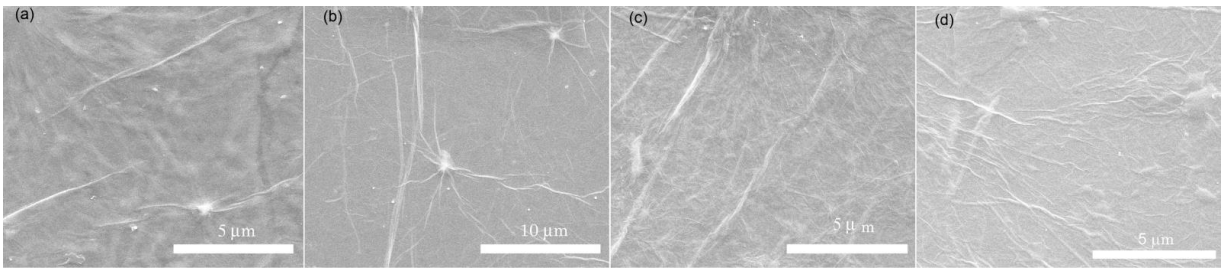
**Supplementary information**




**SFIG 1:** SEM images of (a) GO, (b) rGO3, (c) rGO6 and (d) rGO9

**SBOX 1:** UV-reduction mechanism

Oxygen leaves the surface via $CO_2$, CO while $H_2$ can also be expected during the reduction process,[1-3] which requires the presence of epoxy and carboxyl groups. Another explanation of shift in lower binding energy side lies in the mechanisms of oxygen bearing functional group depletion form the carbocation it bounded. OH, CO and $CO_2$ depletion from aromatic ring suggest depletion by giving one electron to carbocation in the ring. (see reactions 1, 2 as given in Ref. [2])

$$(GO)–COOH \rightarrow GO^{\bullet} + H_2O+CO_2 (\uparrow) \text{ ---------- (1)}$$

$$(GO)–C–O–C \rightarrow GO^{\bullet} + H_2O + CO (\uparrow) \text{ ---------- (2)}$$

These radicals then react with other carbon atoms rebuilding $sp^2$ cluster or disordered ring.

Another study proposed the following mechanism for depletion of oxygen bearing functional groups. This includes contribution from both electrons and holes created upon photo excitation.[1] See the reactions 3-6 as given in Ref.[1]

$$(GO)–C–O–C + 2h^+ + H_2O \rightarrow (GO)–C_{(defect)} + CO_2 + 2H^+ \text{ ---------- (3)}$$

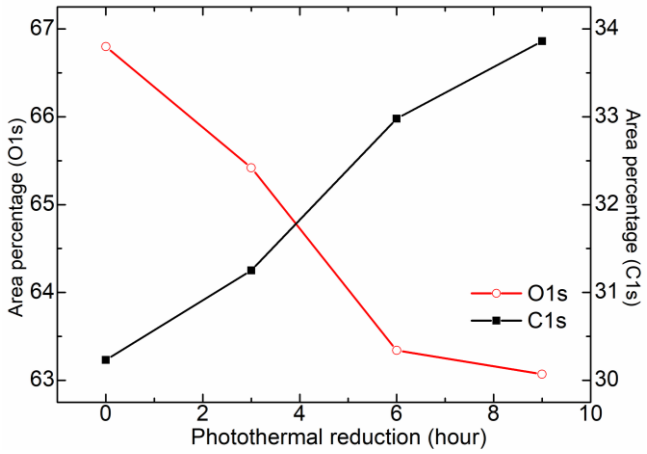
OR

$$(GO)–C–O–C + 2e^- + 2H^+ \rightarrow (GO)–C_{(defect)} + CO_2 + H_2O \text{ ---------- (4)}$$

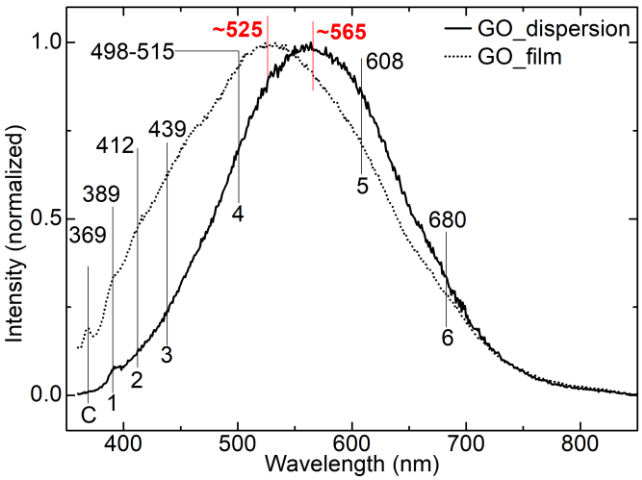
$$C–OH + 3h^+ + H_2O \rightarrow (GO)–C_{(defect)} + CO_2 + 3H^+ \text{ or ---------- (5)}$$

OR

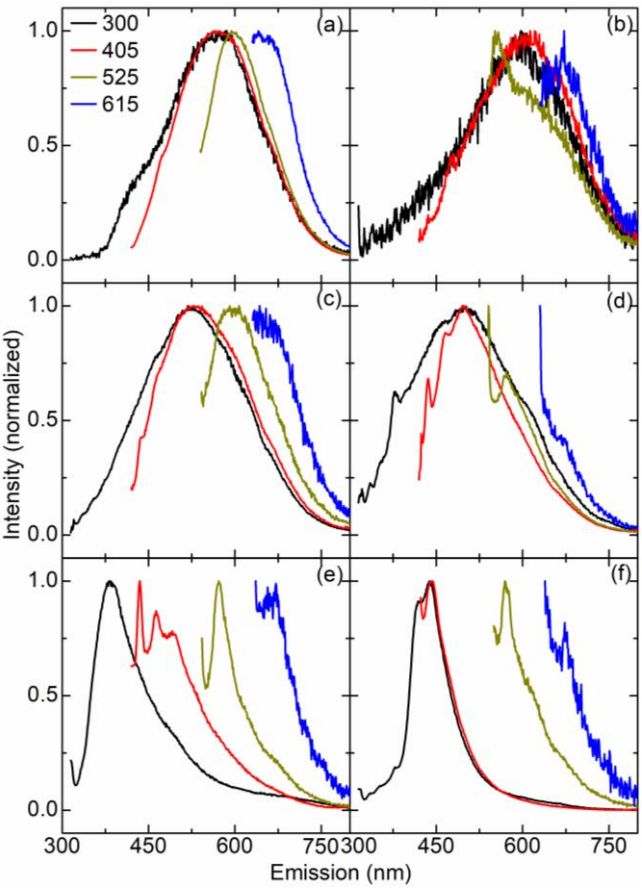
$$C–OH + e^- + H^+ \rightarrow (GO) –C_{(defect)} + CO_2 + H_2O \text{ ---------- (6)}$$



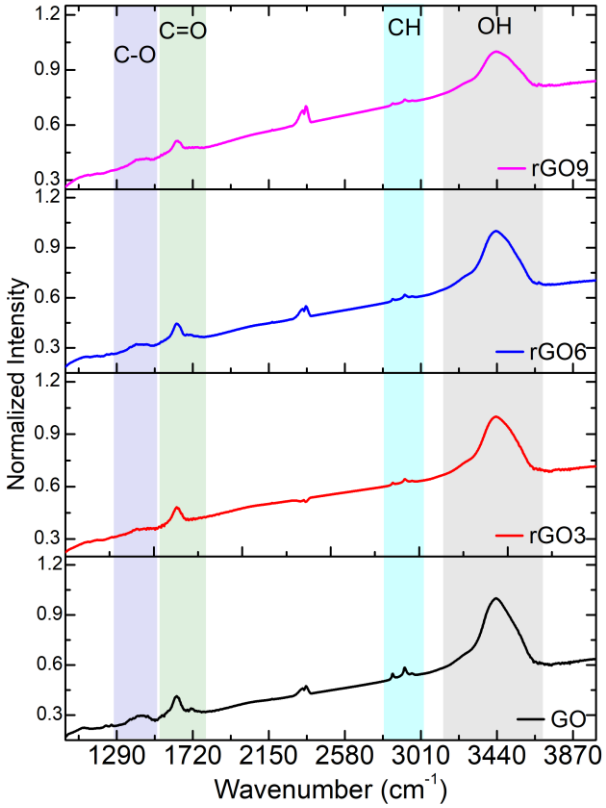

**SFIG 2. Area percentage of C and O content from XPS survey spectra for as prepared GO and after reduction for 3 hours (rGO3), 6 hours (rGO6) or 9 hours (rGO9).**




**SFIG 3. Comparison of fluorescence spectra from dispersion and film samples GO. Spectral positions are annotated in the units of nm.**




**SFIG 4: Four selected excitation wavelengths depicting fluorescence spectra from dispersion of (a) GO, (b) rGO3 and films of (c) GO, (d) rGO3, (e) rGO6 and (f) rGO9 on normalized scale.**




**SFIG 5: FTIR spectra from GO and rGO samples after background subtraction.**

**STAB 1: Peak intensity ratios from FTIR spectra for –OH, C-O and C=O functional groups.**

| Ratio details | Functional group | Peak position ($cm^{-1}$) | Sample name | | | |
|---|---|---|---|---|---|---|
| | | | GO | rGO3 | rGO6 | rGO9 |
| Area ratio | $(OH)_{v1}$ | 3250 | 1 | 0.63 | 0.76 | 0.44 |
| | $(OH)_{v2}$ | 3440 | 1 | 0.85 | 0.87 | 0.56 |
| | $(OH)_{v3}$ | 3562 | 1 | 1.01 | 1.01 | 0.68 |
| Height ratio | $(CH)_{v1}$ | 2921 | 1 | 0.41 | 0.31 | 0.18 |
| | $(CH)_{v2}$ | 2848 | 1 | 0.51 | 0.11 | 0.11 |
| | $(C=O)_{v}$ | 1630 | 1 | 0.79 | 0.86 | 0.39 |
| | $(C-O)_{v}$ | 1430 | 1 | 0.15 | 0.31 | 0.15 |

**References**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3. I. Jung, D. A. Field, N. J. Clark, Y. Zhu, D. Yang, R. D. Piner and R. S. Ruoff, *J Phys Chem C*, 2009, **113**, 18480-18486.