

Photochemical Reactivity of Graphene

Supporting Information

*Haitao Liu, Sunmin Ryu, [□] Zheyuan Chen, Michael L. Steigerwald, Colin Nuckolls,
and Louis E. Brus*

Department of Chemistry, and the Columbia University Center for Electronics of
Molecular Nanostructures, Columbia University, 3000 Broadway, New York, New York, 10027

[□] Present address: Department of Applied Chemistry, Kyung Hee University, 1 Seocheon
Kiheung, Yongin, Kyungki, 446-701, Korea

Complete Reference 5 (b):

Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z. Y.; De, S.; McGovern, I. T.; Holland, B.; Byrne, M.; Gun'ko, Y. K.; Boland, J. J.; Niraj, P.; Duesberg, G.; Krishnamurthy, S.; Goodhue, R.; Hutchison, J.; Scardaci, V.; Ferrari, A. C.; Coleman, J. N. *Nature Nanotech.* **2008**, *3*, 563-568.

Photochemical Reaction between Graphene and Benzoyl Peroxide

Single and few layer graphene were prepared by mechanical exfoliation of Kish graphite (Covalent Materials) onto Si wafer having 300 nm of thermal oxide.¹ The thickness of the graphene was determined using Raman spectroscopy. The graphene on the Si wafer was

immersed in a quartz UV-Vis cuvette that was filled with benzoyl peroxide solution (5 – 20 mM in toluene). Photochemical reaction was carried out by focusing a laser beam (Ar-ion: 458 nm, 514 nm; He-Ne: 633 nm) onto the graphene flake using an inverted microscope fitted with a 40 x (NA: 0.60, with correction ring for coverslip thickness compensation) extra long working distance objective and an x-y translational stage. The spot size is $\sim 0.5 \mu\text{m}$. The laser power was measured above the objective with a laser power meter. Typical power was 0.4 mW. The defect formation can be observed at a power level as low as $4 \mu\text{W}$ (514 nm) if given enough exposure time.

Raman Spectroscopy

Raman spectrum was collected in a backscattering geometry, using a home build micro-Raman setup that consists of the aforementioned inverted microscope, a holographic notch filter, and a single stage 0.27-m spectrograph fitted with a liquid N₂ cooled CCD camera. Integration time ranges from 1 min to 1 hour, depending on the laser intensity.

AFM Imaging

Tapping mode AFM image was acquired using a Digital Instruments Multimode AFM.

Figure S1 shows the AFM image of a graphene flake after the photochemical reaction. The left part of this flake is a double layer while the right part is a single layer. The laser (514 nm, 0.4 mW) was focused onto the single layer as well as onto the boundary between the single and the double layer, as indicated by the green arrows. The reaction time was 20 min for each spot. A hole is clearly visible on the single layer. More interestingly, laser illumination on the single layer – double layer boundary etches away only the single layer region.

Fabrication of Graphene Field Effect Transistor (FET) Devices

Single layer graphene was identified with an optical microscope and confirmed with Raman spectroscopy. PMMA (950K C5, MicroChem) was spin coated onto the wafer (3k rpm, 45 s). The wafer was baked on a hot plate at 180 °C for 2 min. Marks were patterned onto the PMMA film using an e-beam lithography system that consists of an FEI field emission SEM and a NPGS system. The marks were developed in PMMA developer (3/1 IPA/MIBK, MicroChem) for 90 s. The graphene flake was located relative to the marks with an optical microscope. Electrodes were then patterned onto the graphene flake using the existing PMMA layer as the resist and developed with 3/1 PMMA developer. A thin film of Au (50 nm) with 5 nm of Cr adhesion layer was evaporated onto the substrate using a thermal evaporator. Lift-off was achieved by immersing the wafer in a CH₂Cl₂ solution overnight. Figure S2 shows the optical image of two finished FET devices.

Thermal Reaction between Graphene and Benzoyl Peroxide

In one experiment, a Si wafer with a pristine single layer graphene was immersed in a glass vial that was filled with a toluene solution of benzoyl peroxide (20 mM). The vial was heated on a hotplate at 100 °C for 45 min. The half life of benzoyl peroxide is ~ 1 hr at 92 °C. The Si wafer was rinsed with toluene, acetone, and isopropanol and dried with a stream of nitrogen. The graphene flake was characterized with micro Raman spectroscopy (Figure S7A). No significant D band was observed.

In another experiment, a single layer graphene was photochemically modified with a focused 514 nm laser beam. The region that has been exposed to the laser showed strong D band in the Raman spectrum. After the photochemical reaction, the Si wafer with the graphene flake was immersed in a glass vial that was filled with a toluene solution of benzoyl peroxide (20 mM). The vial was heated to 110 °C in an oil bath for 86 min. The wafer was then rinsed with

isopropanol, acetone, water, and isopropanol again. The wafer was dried with a stream of nitrogen and the graphene flake was characterized with Raman spectroscopy. Figure S7B compares the Raman spectrum taken from the region that has been previously exposed to the laser beam before the thermal reaction (red curve) and the spectrum taken from the region that has not been exposed to laser (black curve). It is clear that the region that has not been exposed to laser irradiation remains defect free after the thermal reaction.

Note: It is essential that the graphene flake is thoroughly rinsed before the Raman spectrum is taken. We observed growing D band in the Raman spectrum if the graphene flake was not carefully rinsed after the thermal reaction. Such D band formation is attributed to the photochemical reaction of the residue benzoyl peroxide adsorbed on the graphene surface.

Wavelength Dependence of the Reaction Kinetics

The same piece of graphene flake was used to compare the effect of laser wavelength on the reaction kinetics.

514 nm vs 458 nm. The reaction was carried out on two spots of a single layer graphene. The two spots are several micrometers away to minimize possible interference. The single layer graphene was immersed in a solution of benzoyl peroxide in toluene (5 mM). The photochemical reaction was carried out using the 514 nm line and the 458 nm line of an Ar-ion laser. The laser power used for both wavelengths was 0.4 mW. For this set of experiments, the Raman spectrum collected with the 458 nm laser was rather weak, presumably due to the difference of the instrument response at the two wavelengths. We used the time evolution of the 2D band to characterize the kinetics of defect formation (Figure S8). The decay of the 2D band was about 5 times faster with the 458 nm line than with the 514 nm line.

514 nm vs 633 nm. The reaction was carried out on two spots of the same single layer graphene. The two spots are several micrometers away to minimize possible interference. The single layer graphene was immersed in a solution of benzoyl peroxide in toluene (10 mM). The photochemical reaction was carried out using the 514 nm line of an Ar-ion laser and using the 633 nm line of a He-Ne laser. This graphene flake was much more reactive than almost all the other ones we have studied, presumably due to a higher density of natural defects. With 514 nm laser (0.4 mW), we observed an I_D/I_G ratio of about 1 within the first minute of the laser irradiation, where I_D and I_G are intensities of the D and G bands, respectively (Figure S9). The reaction using the 633 nm line (0.8 mW) developed a similar I_D/I_G ratio in about 25 min. The focused spot of the 633 nm laser beam ($\sim 1\mu\text{m}$) is about twice larger than the focused spot of the 514 nm beam ($\sim 0.5\mu\text{m}$); the ratio of the light intensity in the laser focus is about 2 : 1 (514 nm : 633 nm). We thus conclude that the kinetics is about 10 times (12.5 times to be exact) slower using the 633 nm laser than using the 514 nm laser.

Raman spectrum of single-layer graphene in the presence of biphenyl. A single-layer graphene on Si/SiO₂ substrate was immersed in a UV cuvette that was filled with a solution of biphenyl in toluene (10 mM, 99%, Aldrich). Raman spectrum (Figure S12) was collected as described in the supporting information. Each spectrum was integrated for 5 min at a power level of 0.4 mW (514 nm). No change in the Raman spectrum was observed over 20 min of laser illumination and no D band was observed. In contrast, it only takes 3 min of laser illumination (0.4 mW, 514 nm) to produce significant D band on a single-layer graphene that was immersed in a toluene solution of benzoyl peroxide (5 mM, see Figure 3 of the main text). This experiment shows that the D band observed in the photochemical reaction is not due to the pi-pi interaction between biphenyl and graphene.

Estimate of the Reactivity Difference between Single Layer and Double Layer Graphene

We assume that 1) the D band intensity of a graphene layer is not affected by the presence of a neighboring layer, and 2) only the top layer of a double layer graphene reacts. In figure 3, the single layer and the double layer graphene developed about the same absolute D band intensity at ~ 4 min and ~ 56 min, respectively. Thus the reactivity of the double layer graphene is about 14 times lower than that of the single layer graphene. Our method of estimating the reactivity difference is slightly different from the one used in the hydrogenation study.²

Estimate of the Quantum Yield

An order-of-magnitude estimation of the defect density on graphene can be made based on the simulated Raman spectra of hydroxylated graphene.³ Evenly distributed 1, 2 - hydroxyl pairs with OH density of $4.8 \times 10^{14} / \text{cm}^2$ (0.13 monolayer) was predicted to produce an I_D/I_G ratio of about 1.^{2,3}

Under 0.4 mW of 514 nm laser irradiation, the I_D/I_G ratio of the graphene sample reaches about 1 in ~ 5 min (Figure 3A). The quantum yield (QE) of the defect formation can be calculated as the following:

$$QE = \frac{N_{\text{Defect}}}{N_{\text{Photon}}} = \frac{n_{\text{Defect}} \times \text{Area}}{P \times \text{Abs}_{\text{Graphene}} \times t \div h \frac{c}{\lambda}} = \frac{(0.5 \times 10^{-4} \text{ cm})^2 \times 4.8 \times 10^{14} \text{ cm}^{-2}}{0.4 \times 10^{-3} \text{ W} \times 300 \text{ s} \times 0.023 \div (6.63 \times 10^{-34} \times \frac{3 \times 10^8}{514 \times 10^{-9}})}$$
$$= 1.7 \times 10^{-10} \text{ defects / photon}$$

Where N_{Defect} , N_{Photon} , n_{Defect} , Area , P , $\text{Abs}_{\text{Graphene}}$, t , h , c , and λ are the number of defects, the number of photons, the defect density at 5 min of reaction ($4.8 \times 10^{14} / \text{cm}^2$), the area within the laser focus ($0.5 \mu\text{m} \times 0.5 \mu\text{m}$), the power of the laser (0.4 mW), the optical absorption of single

layer graphene at 514 nm (~ 0.023),⁴ the time of the reaction (300 s), the Plank constant (6.63×10^{-34} J·s), the speed of light, and the wavelength of the laser (514 nm), respectively.

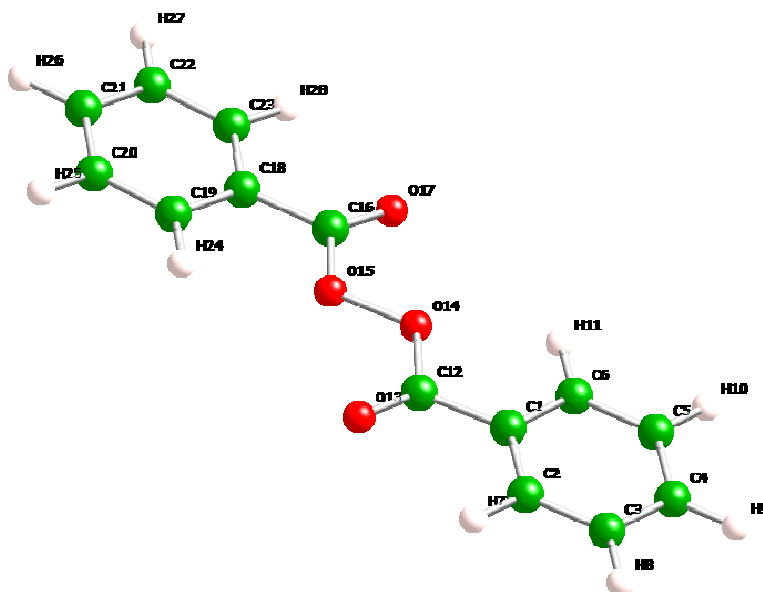
DFT Calculations

All calculations were performed using Jaguar, version 7.0, Schrodinger, LLC, New York, NY, 2007. The hybrid functional B3LYP was used throughout. The geometries of benzoyl peroxide and *t*-butyl peracetate were optimized using the 6-31G** basis set; these optimized geometries are given below.

Using these optimized geometries and the 6-311++G** basis set, we calculated the energies of the neutral molecules and the corresponding radical anions to give an estimate of the gas-phase vertical electron affinities. The results are summarized below:

Energy	Benzoyl Peroxide	<i>t</i> -butyl peracetate
Neutral Molecule (Hartree)	-840.56600	-461.60155
Radical Anion (Hartree)	-840.58997	-461.57798
Gas-phase vertical electron affinity (kcal/mol)	15.04	-14.79

At this level of calculation the radical anion of benzoyl peroxide is weakly bound, but the radical anion of *t*-butyl peracetate is unbound with respect to the neutral molecule and a free electron. In both cases the optimized (fully relaxed) geometry of the radical anion gives a broken O-O bond leaving a carboxylate anion and a benzoyloxyl radical and a *t*-butoxy radical, respectively.

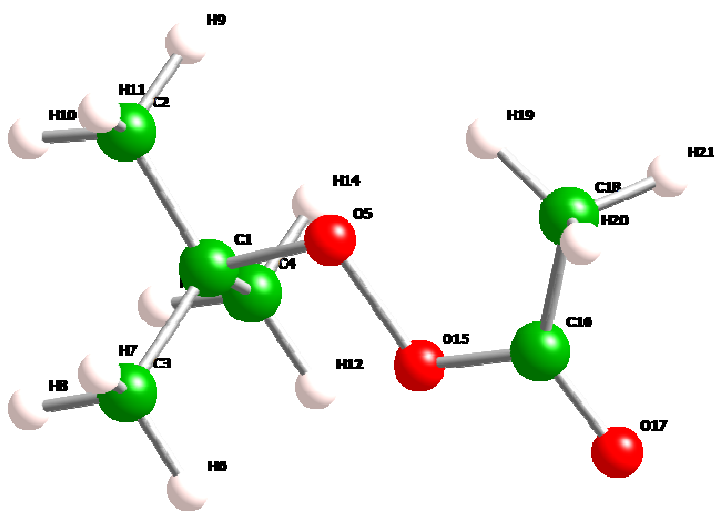


Optimized Geometry of Benzoyl Peroxide

Final geometry (Å):

atom	x	y	z
C1	0.0441725238	-0.0006920496	-0.1805311829
C2	-0.0705937568	-0.0241785847	1.2150500226
C3	1.0686505237	-0.1640079886	2.0021386851
C4	2.3233801363	-0.2811374148	1.4004836475
C5	2.4393564724	-0.2587396436	0.0093768344
C6	1.3049557668	-0.1190081398	-0.7853682082
H7	-1.0558896309	0.0676852850	1.6594415117
H8	0.9793082322	-0.1820075715	3.0840188841
H9	3.2114779012	-0.3905162186	2.0162939380
H10	3.4150642212	-0.3508043224	-0.4577636774

H11	1.3929056093	-0.1030672847	-1.8656531912
C12	-1.2145962868	0.1496154332	-0.9645804697
O13	-2.3348052639	0.2341904575	-0.5301895477
O14	-0.8855363165	0.1795344686	-2.3026915925
O15	-2.0745994928	0.3095870620	-3.1004230998
C16	-1.6966797003	0.2352663589	-4.4282940072
O17	-0.5606371157	0.0788618083	-4.7981803674
C18	-2.8934691942	0.3776060350	-5.3008206602
C19	-4.1921595165	0.5640893448	-4.8062887186
C20	-5.2546888117	0.6903191398	-5.6982045445
C21	-5.0284298439	0.6313038959	-7.0747378316
C22	-3.7347578096	0.4450707005	-7.5665369770
C23	-2.6684325855	0.3184564899	-6.6827965480
H24	-4.3660333489	0.6092694126	-3.7369492364
H25	-6.2612748615	0.8352263052	-5.3182148343
H26	-5.8614254172	0.7307324538	-7.7647366827
H27	-3.5588804309	0.3991241528	-8.6369207649
H28	-1.6542294084	0.1738182270	-7.0387618572



Optimized Geometry of *t*-butyl Peracetate

Final geometry (Å)

atom	x	y	z
C1	0.0269999572	-0.0479452069	-0.0434284985
C2	-0.0283068776	0.0489219035	1.4863433448
C3	1.4714749451	-0.0095356491	-0.5522671242
C4	-0.7338330889	-1.2765082185	-0.5519553999
O5	-0.6708669447	1.1672964694	-0.4266351869
H6	1.5005750518	-0.0168223361	-1.6437861679
H7	1.9769061290	0.8935149600	-0.1976865342
H8	2.0234421158	-0.8812489258	-0.1872784999
H9	-1.0634451213	0.0657486290	1.8384358436

H10	0.4720077417	-0.8197466487	1.9239765980
H11	0.4771337036	0.9526814984	1.8377747776
H12	-0.7415059433	-1.3060705921	-1.6434458014
H13	-0.2593766833	-2.1923420679	-0.1860210527
H14	-1.7687617559	-1.2577054999	-0.1980056063
O15	-0.6894910876	1.2033409772	-1.8975486469
C16	-1.3306144556	2.3057543672	-2.3971146333
O17	-1.3725495159	2.3828845532	-3.6008874663
C18	-1.9238997544	3.3205089700	-1.4506763685
H19	-1.7856406039	3.0763026391	-0.4011292885
H20	-1.4681897534	4.2891732175	-1.6734104574
H21	-2.9899842148	3.4042895362	-1.6788186741

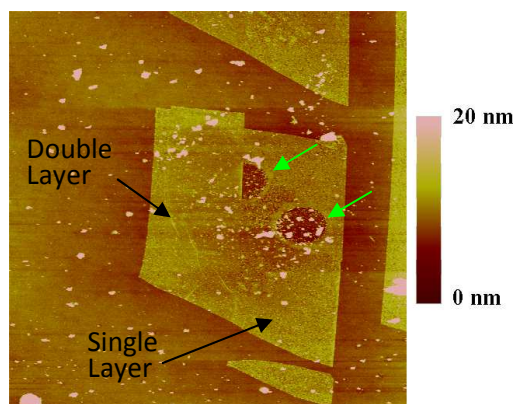


Figure S1. Tapping mode AFM image of a graphene flake after the photochemical reaction (514 nm, 0.4 mW, 20 mM of benzoyl peroxide in toluene). Green arrows indicate location of laser focuses. Scan size: 15 μm .

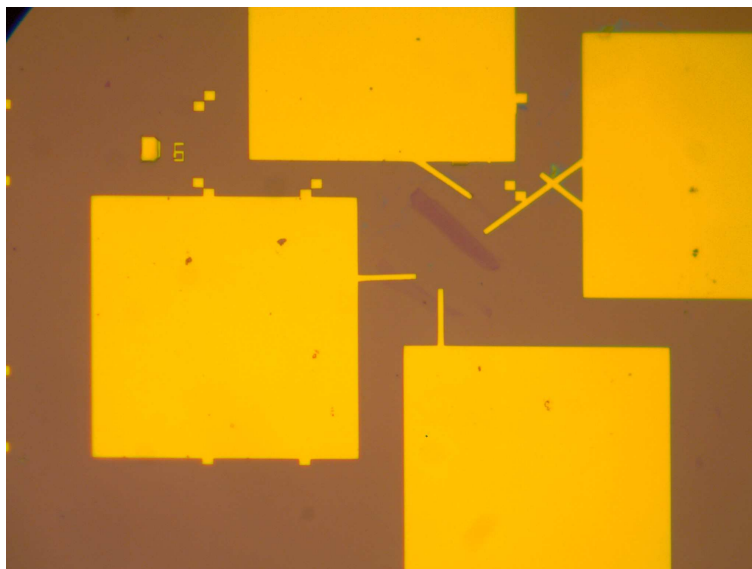


Figure S2. Optical image of two graphene FET devices. The sides of the square electrode pads are $\sim 100 \mu\text{m}$ in length.

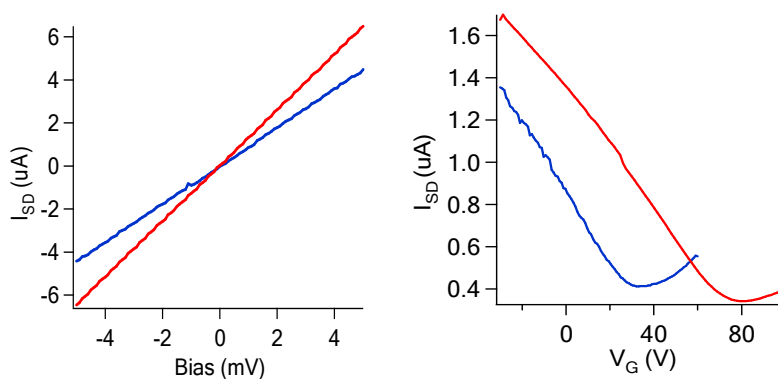


Figure S3. (Left) Output and (Right) transfer characteristics ($V_{SD} = 1 \text{ mV}$) of the same single layer graphene FET device before (blue) and after (red) being immersed in a toluene solution of benzoyl peroxide. This device was not exposed to laser illumination.

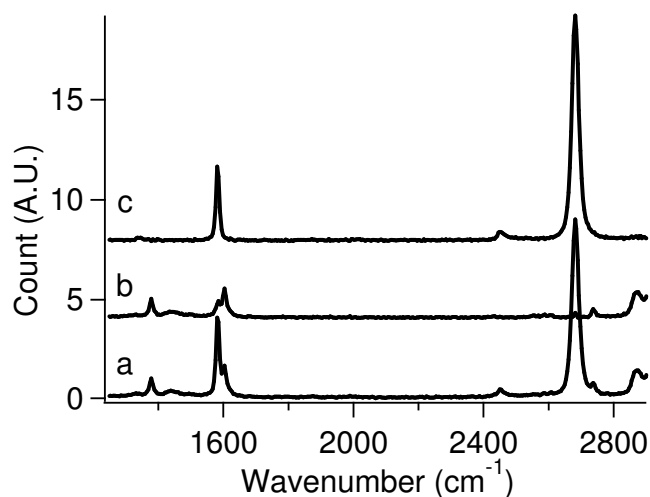


Figure S4. (a) Raman spectrum ($\lambda_{\text{ex}} = 514 \text{ nm}$, 0.4 mW, 5 min) of a single layer graphene immersed in pure toluene at ambient atmosphere. The spectrum was taken after the graphene was irradiated with focused 514 nm laser for 10 min ($\lambda_{\text{ex}} = 514 \text{ nm}$, 0.4 mW, 5 min). (b) Raman spectrum of the Si/SiO₂ substrate in toluene. (c) (a) – (b). No significant D band is observed.

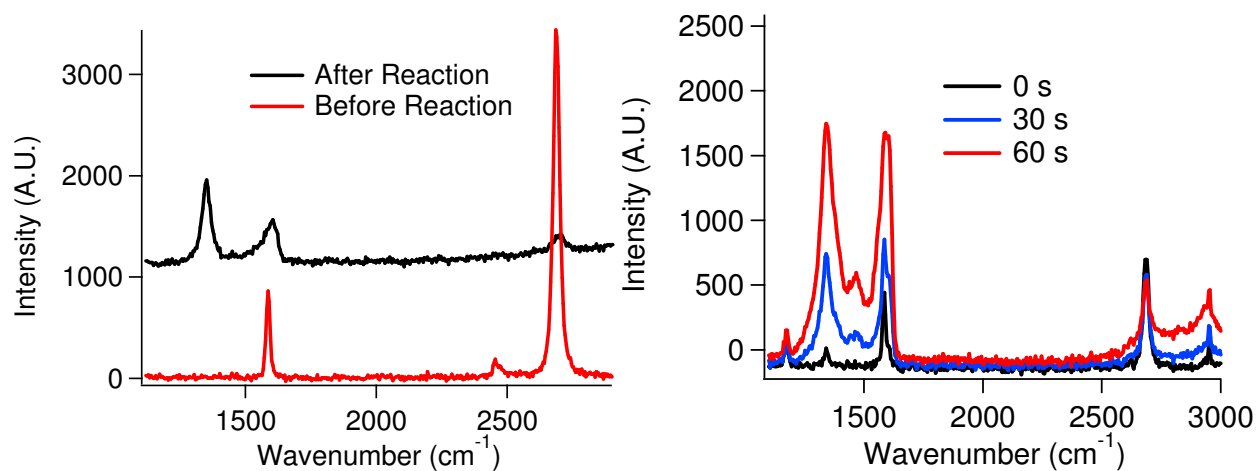


Figure S5. (Left) Raman spectrum of a single layer graphene (514 nm, 0.4 mW) before and after reacting with a saturated solution of *p*-nitro benzoyl peroxide in CCl₄ under 514 nm photoexcitation. (Right) Time evolution of the Raman spectrum of a single layer graphene reacting with benzoyl peroxide solution in benzene (5 mM) under 514 nm photoexcitation (0.4 mW).

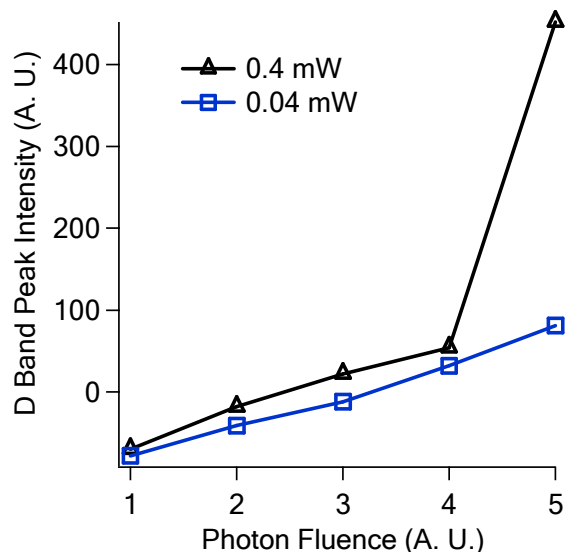


Figure S6. Time evolution of the D band peak intensity for a single layer graphene immersed in a toluene solution of benzoyl peroxide (20 mM) and illuminated with 0.4 mW (Black) and 0.04 mW (Blue) laser (514 nm). The exposure time was adjusted accordingly to obtain the same photon fluence for the two experiments. The rate of the D band growth with respect to the photon fluence is essentially the same within the first 4 data points. A. U.: arbitrary unit.

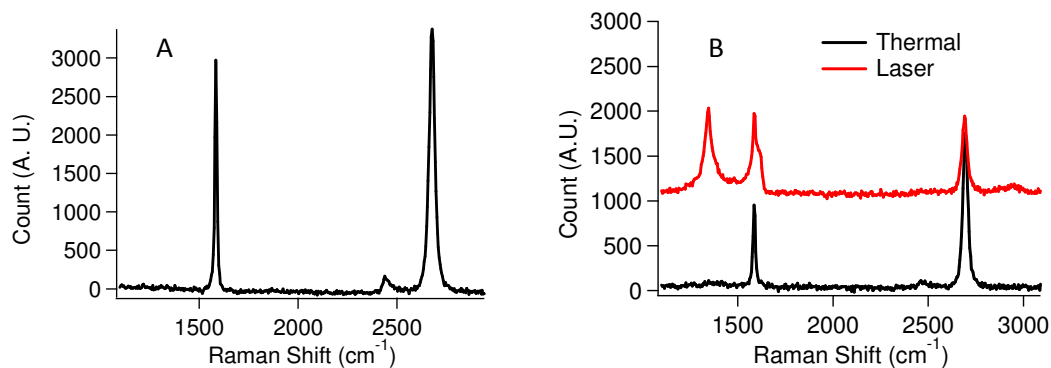


Figure S7. (A) Raman spectrum (514 nm, 0.4 mW, 5 min integration) of a pristine single layer graphene that has been reacted with a toluene solution of benzoyl peroxide (20 mM) at 100 °C for 45 min. Spectrum taken in air. (B) Raman spectra (514 nm, 0.4 mW, 90 s integration,

spectrum taken in air and shifted for clarity) on two different spots of a single layer graphene that has been reacted with benzoyl peroxide (20 mM) at 110 °C for 86 min. Prior to the thermal reaction, part of this graphene flake was illuminated with a focused 514 nm laser beam to induce localized defect formation. The region that was exposed to laser remains defect rich after the thermal reaction (red curve). However, the region that has not been exposed to laser did not develop D band during the thermal reaction with benzoyl peroxide (black curve). A. U.: arbitrary unit.

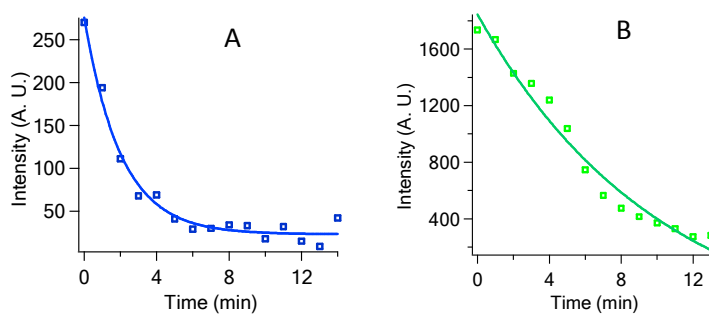


Figure S8. Time evolution of the 2D band peak intensity on two different spots of the same single layer graphene immersed in benzoyl peroxide (5 mM) solution in toluene. Photochemical reaction was initiated by illuminating with (A) 458 nm laser (0.4 mW) and (B) 514 nm laser (0.4 mW). The decay of the 2D band indicates the defect formation and oxidative etching of the

graphene basal plane. The dots are experimental data and the lines are fits to single exponential.

$k_{\text{obs}} = 0.49 \pm 0.05 \text{ min}^{-1}$ (458 nm), $k_{\text{obs}} = 0.099 \pm 0.030 \text{ min}^{-1}$ (514 nm). A. U.: arbitrary unit.

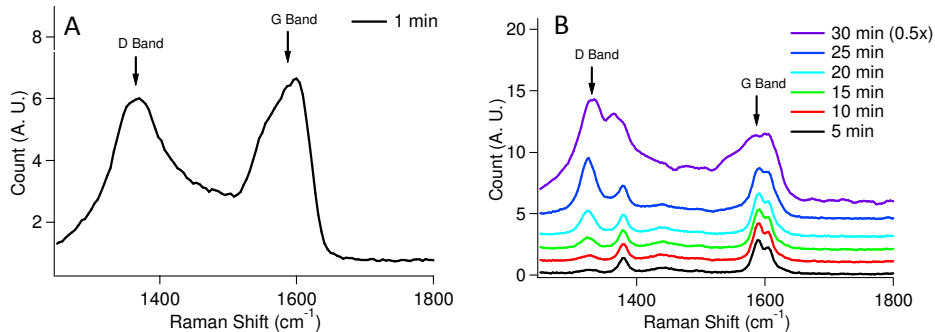


Figure S9. Raman spectrum of two different spots of the same single layer graphene illuminated with (A) 514 nm, 0.4 mW and (B) 633 nm, 0.8 mW. This graphene flake was immersed in a 10 mM of benzoyl peroxide solution in toluene. The peaks near 1368 cm^{-1} and 1600 cm^{-1} in (B) are from toluene. A. U.: arbitrary unit.

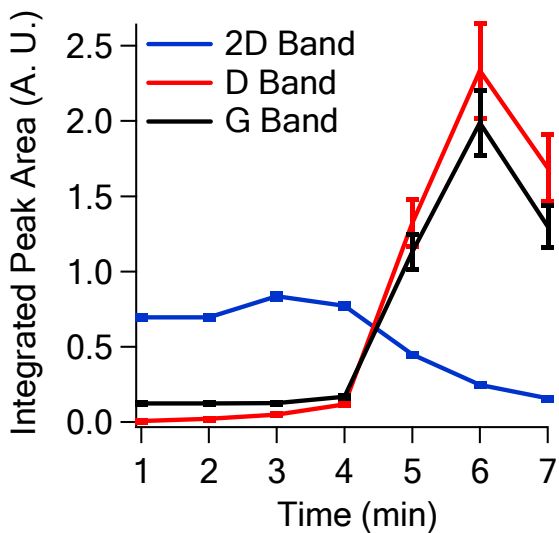


Figure S10. Time evolution of the integrated intensity of the D, G, and 2D bands. A. U.: arbitrary unit.

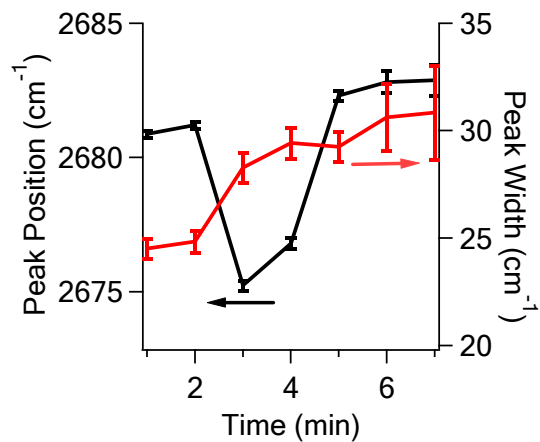


Figure S11. Time evolution of the peak position and width of the 2D bands.

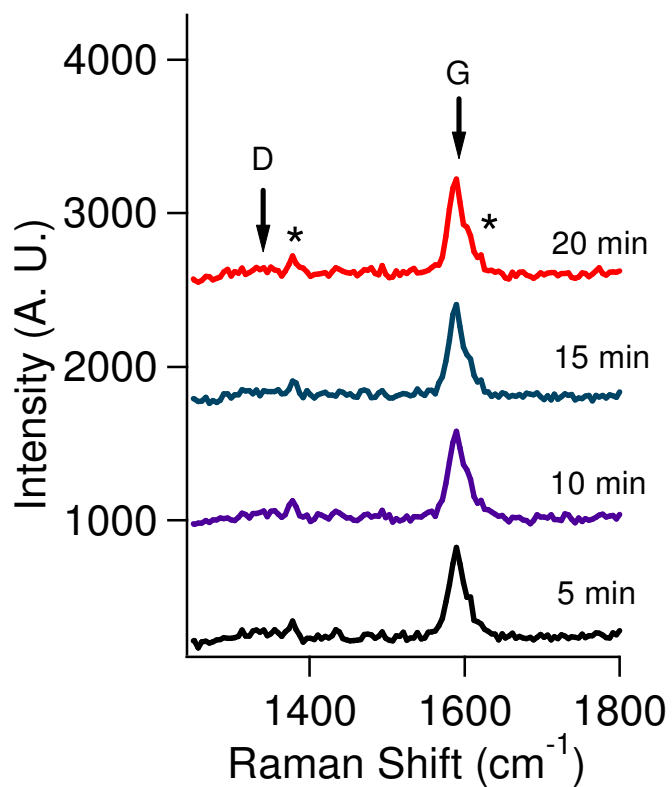


Figure S12. *in-situ* Raman spectra of a single-layer graphene immersed in a solution of biphenyl in toluene (10 mM). (*) indicates Raman peaks of toluene.

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