**Supplementary Information** 

Patterning and tuning of electrical and optical properties of graphene by laser induced two-photon oxidation

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## **Experimental methods**

#### FWM imaging

The laser pulses for FWM imaging experiments were produced by two non-collinear optical parametric amplifiers (NOPAs, Orpheus-N, Light Conversion) pumped by an amplified femtosecond laser (Pharos-10, 600 kHz, Light Conversion). The two output pulses can be tuned independently from 510 nm to 890 nm and the typical pulse duration in the visible range is ~30 fs. We used 540 nm and 590 nm wavelengths in which case their energy difference matches the G-band frequency of the graphene. The group velocity dispersion induced by transmitting optics was compensated with an additional prism compensator (fused silica prism pair) yielding a pulse duration of ~40 fs at the sample. Relative time delays of the two laser pulses were adjusted with computer controlled optical delay lines (Thorlabs). For imaging, the pulses were overlapped in time. The two beams were attenuated independently with variable neutral density filters before aligning them to collinear geometry by using beam splitters. An additional variable neutral density attenuator was installed in the path of the combined beam in order to adjust the laser power without changing the relative intensity of the two pulses. A tube lens and a camera were installed behind a beamsplitter to view the laser spots on the sample.

Laser beams were focused to the sample by a microscope objective (Nikon LU Plan ELWD 100x/0.80). The sample was installed to a closed chamber that was purged with nitrogen or argon gas during imaging to prevent oxidation of the graphene. The sample chamber was attached on a three-axis piezo-stage (Thorlabs NanoMax 300) to control the position of the sample. FWM signal was collected to backscattering direction and separated from the input beams with dichroic long-pass filter (Semrock) and further purified from the residuals of the input beams by using a

bandpass filter (Semrock). Spectrally filtered signal was focused to a photon counting module (single photon avalanche photodiode, SPCM-AQRH-14, Excelitas Technologies). Imaging was performed by a point scan method with typical detection times of 0.1-0.2 s/point. The intensity of the laser radiation at the sample was typically from 5 x  $10^{10}$  to 2 x  $10^{11}$  W/cm<sup>2</sup>.



Schematic of the laser setup used for patterning and FWM imaging. NOPA = non-collinear optical amplifier, PC = prism compressor, M = microscope, D = detector.

### Photo-oxidation

Local photo-oxidation of the graphene was carried out with the same laser setup as FWM imaging. During oxidation inert gas purge was switched off and the sample chamber contained ambient atmosphere. Patterns were oxidized by moving the sample in 100 nm steps and the position and the irradiation time of each oxidation point was computer controlled. Typical intensities for oxidation were from  $1 \times 10^{11}$  to  $1 \times 10^{12}$  W/cm<sup>2</sup>.

#### Raman spectroscopy

Raman measurements were carried out with a home-built Raman setup<sup>1</sup> in a backscattering geometry using 532 nm excitation wavelength produced with CW single frequency laser (Alphalas, Monolas-532-100-SM). The beam was focused to a sample, and subsequently collected, with a 100x microscope objective (Nikon L Plan SLWD 100x with 0.70 N.A.). The scattered light was dispersed in a 0.5 m imaging spectrograph (Acton, SpectraPro 2500i) using 600 g/mm grating (resolution:  $\sim$ 3 - 4 cm<sup>-1</sup>). The signal was detected with EMCCD camera (Andor Newton EM DU971N-BV) using 100 µm slit width. A beam splitter was placed between the objective and the spectrometer in order to observe the exact measurement point visually. The Rayleigh scattering was attenuated with an edge filter (Semrock). The approximate sample positioning was done manually with XYZ-stage (Newport, ULTRAling 462-XYZ-M) and fine – tuned with XYZ-piezoscanner (Attocube, ANPxyz101) with smallest step of 50 nm in each direction. Laser power of ~5 mW was utilized and two 30 s measurements were averaged for each accumulation.

#### SEM-EDX Measurements

Scanning electron microscope (SEM) measurements and energy-dispersive x-ray (EDX) analysis for carbon (K-electrons) and oxygen (K-electrons), were performed using FEI QUANTA microanalysis system with Zeiss EVO 50 scanning electron microscope and Bruker AXS XFlash Detector 3001. The applied acceleration voltage was 7.53 kV.

#### Samples for electronic transport measurements

P-doped Si wafers with 300 nm SiO<sub>2</sub> and a monolayer of graphene, where the graphene was grown by CVD on Cu and transferred to the wafer, were bought from Graphenea SA, 20018 Donostia-San Sebastia'n, Spain. Electrodes of Ti (2nm) and Pd (25 nm) were defined on top of the graphene, using electron beam lithography and physical vapor deposition. Then suitable graphene structures were defined between the electrodes, using electron beam lithography and reactive ion etching (oxygen plasma).

#### Electronic measurements.

All electronic measurements were conducted at room temperature in ambient conditions. The measurements were computer-controlled, using LabView. The drain-source and gate-source dc voltage bias was supplied through a shielded rack-mountable connector block (National Instruments BNC-2090). The current response through the graphene device was monitored, using a current preamplifier (Stanford Research Systems, SR570). A drain-source bias of 100 mV was used during the transfer characteristics measurements.

## Two-photon cross-section for oxidation

Two-photon cross-section for the photo-oxidation reaction is calculated by using the equations presented by Koester et al.<sup>2</sup> We assume that the process consists of two-photon excitation which leads to oxidation with a quantum yield of 1. The cross-section is derived by fitting FWM signal decay constant as a function of laser power squared (Fig. S5). By using the following equation

$$k_2 = \frac{g_p}{\tau f} \left( \frac{\overline{P} \pi (NA)^2}{hc\lambda} \right)^2 \sigma_2$$

where,

 $g_p = 0.664$  (Temporal coherence, We assume gaussian temporal profile)

- $h = 6.626 \text{ x } 10^{-34} \text{ Js}$  (Planck's constant)
- $c = 2.998 \text{ x } 10^{10} \text{ cm/s}$  (Speed of light)
- $\lambda = 540 \text{ x } 10^{-7} \text{ cm}$  (Wavelength)
- f = 600 kHz (Repetition rate)
- NA = 0.8 (Numerical aperture of the focusing objective)
- $\tau = 40$  fs (Pulse duration at the sample)
- P = Measured average laser power at the sample

k = Rate constant at given power from the single exponential fit of the decay of the FWM signal (Figure S4)

we derive that slope of the linear fit 3.93 x  $10^8 = \frac{g_p}{\tau f} \left(\frac{\pi (NA)^2}{hc\lambda}\right)^2 \sigma_2$  and inserting the above listed numerical values we obtain numerical estimation for two-photon cross-section

 $\sigma_2 = 4 \times 10^{-54} \text{ cm}^4 \text{ s photon}^{-1}$ 



**Figure S1.** Raman spectrum of suspended monolayer graphene. The same sample was used in the experiments of Figure 1.



**Figure S2:** Oxidation kinetics of air-suspended monolayer graphene in pure nitrogen (black), air (blue) and pure oxygen (red) atmospheres. The inset shows the kinetics with various mixtures of nitrogen and oxygen. The partial pressures of oxygen are 0 % (black), 1.5 % (red), 5 % (blue), 10 % (cyan) and 21 % (green).



**Figure S3.** Raman spectrum of monolayer graphene. Black spectrum is from unprocessed graphene and red spectrum shows the Raman spectrum after patterning. Patterning induces very strong growth of the D-band, and the G-band shifts up and changes shape. These changes are key signatures of oxidation of graphene.



**Figure S4.** Bar graph of oxygen to carbon ratio in graphene determined by SEM-EDX elemental analysis of air-suspended monolayer graphene. The red bars (a) refer to non-irradiated graphene and black bars (b) correspond to irradiated areas. The measurements for both samples within each sample pair were performed in identical measurement conditions. The oxygen mole fraction increases consistently from ~below 10 % up to ~20 %.



**Figure S5.** Decay kinetics of the FWM signal upon oxidation. The average power in  $\mu$ W is 8 (black), 10 (red), 13 (green) and 16 (blue).



**Figure S6.** FWM signal decay constant as a function of laser power squared. Linear fit indicates second order behavior, i.e. two-photon process.

# References

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- 2. Koester, H. J.; Baur, D.; Uhl, R.; Hell, S. W. Biophys. J. 1999, 77, 2226–2236.