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Electronic Supplementary Information to

Mechanistic insight into light-driven graphene-induced peroxide decomposition: radical generation and disproportionation

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Experimental details

General: The experiments were performed in an ultrahigh vacuum (UHV) chamber evacuated by a combination of ion and turbomolecular pumps. A base pressure below 1.0×10^{-10} torr was reached after baking. The chamber was equipped with an ion sputtering source for surface cleaning, a triple-filter quadrupole mass spectrometer for detecting residual gases as well as desorbing species from the surface, and reflection absorption infrared spectroscopy (RAIRS) for collecting surface vibrational spectra. A 10 mm x 10 mm sample of the CVD grown single layer graphene on copper foil (SLG/Cu) was mounted on a 2 mm thick Au(111) single crystal disk with a diameter of 12.5 mm (see the inset of Fig. S1). The SLG/Cu/Au(111) assembly was fixed to a heating element on a manipulator with capabilities for resistive heating to 1000 K and active cooling to 100 K by liquid nitrogen. A chromel-alumel thermocouple, whose junction was wedged into a hole in the side of the Au crystal, was used to measure the surface temperature (assuming a good thermal contact between SLG/Cu and Au(111)). Programmed heating was achieved by a PID controller to ramp the temperature in a regulated fashion. The temperature-programmed desorption (TPD) experiments were usually started by exposing the SLG/Cu to the vapours of the radical initiator compound at 200 K followed by cooling to 120 K, and the surface was then elevated to 700 K with a linear rate of 1.5 K/s. Upon heating, multiple-ion signals and temperatures were collected synchronously. RAIRS was performed by taking the infrared beam from an FTIR spectrometer and focusing it at grazing incidence (85^{o}) through a ZnSe wire-grid polarizer and a KBr window onto the sample surface in the UHV chamber. The reflected IR beam was then passed through a second KBr window and refocused on a liquid nitrogen cooled HgCdTe detector. All spectra corresponded to the average of 512 scans at 4 cm^{-1} resolution and were ratioed against the background spectra from the clean graphene surface. A clean surface was produced by simply annealing the sample to 700 K for 5 minutes in UHV. No ion bombardment was performed since this can damage the surface integrity or even remove the one-atom thick graphene sheet. The radical reactivity on the single-layer graphene was always regained after the complete removal of the radical reaction products upon 700 K anneal. The experiments were repeated for many times and we believe that the exact nature of graphene remains. Commercially available TBPB (Acros, 98%), DTBP (Aldrich, 98%), *tert*-butabol (TCI, >97%), and isobutylene oxide (TCI, >97%) were purified by several cycles of freeze-pump-thaw prior to use. Gas exposures were quoted as Langmuirs (L), uncorrected for ionization gauge sensitivity and collimator gain factor.

Photochemical: The UV irradiation was accomplished with a LED source (Dr. Honle AG UV Technology, Germany). The LED source provided light in the spectral region of the stated 365±10 nm. Light was brought into the UHV chamber by directly passing through the glass viewport (90% transmittance). The SLG/Cu sample was positioined so that the incident light was normal to the suface and at a distance of 12 cm from the LED source. The intensity was measured to be ~100 mW/cm^2 at this distance by the manufacturer, and the peak intensity was found within an area with a diameter of 10 mm (equivalent to the sample size). No obvious temperature rise was detected when the sample was irradiated at 120 K.

Preparation of graphene by chemical vapour deposition: Graphene samples were grown on 0.035 mm (35μm) thick Cu foil (99.95% purity) in a quartz tube furnace. Under vacuum conditions of 2.6×10^{-1} torr the system was purged with hydrogen (45 sccm) and Ar (10 sccm) gas flows for 10 min, then the temperature of the system was raised from room temperatures to 1050^{o}C in 40 min and aged at that temperature for 20 min under a hydrogen gas flow (45 sccm) only. An Ar (10 sccm) flow was then supplied at the same temperature for another 50 min, followed by a nature cooling to room temperature. Subsequently, the system containing the hydrogen-treated Cu foil was pumped to vacuum. Hydrogen (15 sccm) and methane (10 sccm) flows were introduced for a growth time of 10 min (system pressure was 1.8×10^{-1} torr), and then the system was heated up to 1000^{o}C in 40 min with the flow of hydrogen (15 sccm) only (4.3×10^{-2} torr). After the exposure to hydrogen at 1000^{o}C for 40 min, methane (10 sccm) gas flow was re-supplied for another 30 min growth time along with the hydrogen. A nature cooling was used after growth, and the methane and hydrogen flows were continued throughout the cooling process.

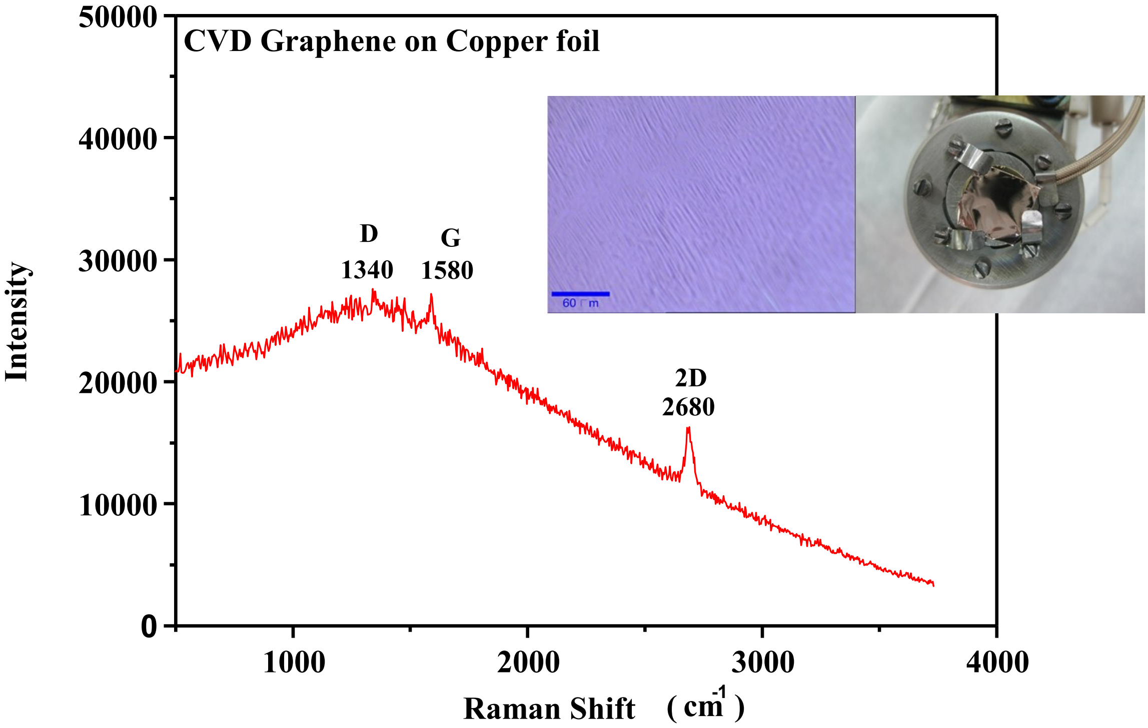

Fig. S1 The single-layer and defect-free nature of gaphene was confirmed by confocal Raman spectroscopy (WITech CRM200) using a laser excitation of 532 nm with a power of 5 mW and 100x objective with a numerical aperature of 0.95 and a standard grating (600 lines/mm). As-grown graphene was charactetrized directly on Cu foil, thus with a strong fluorescence background.

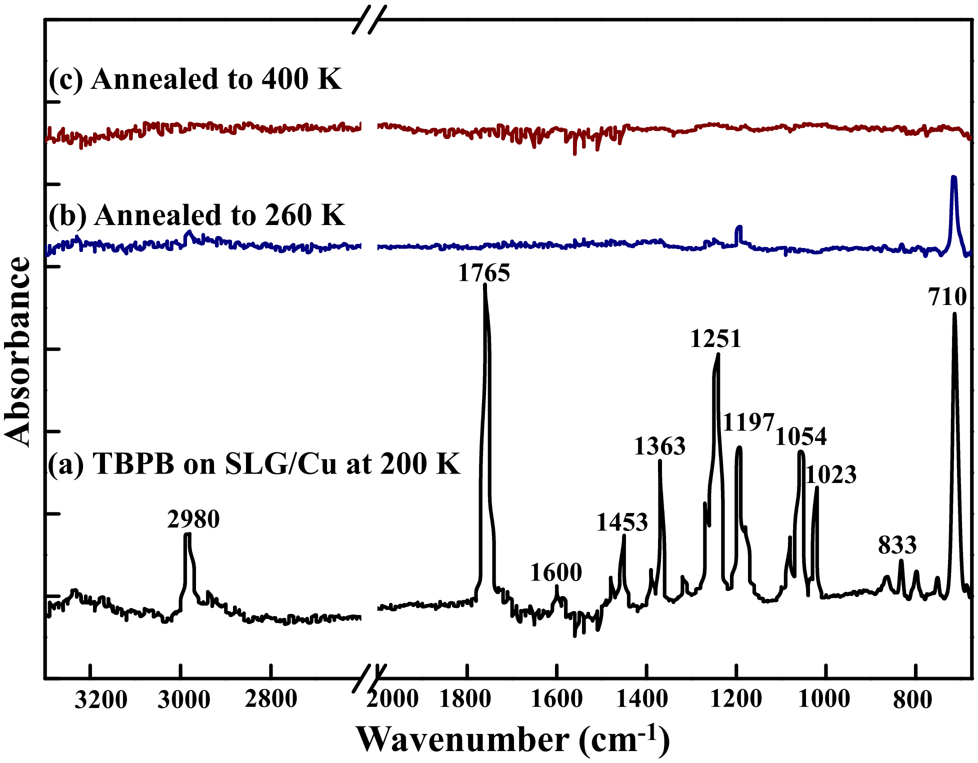

Fig. S2 RAIR spectra of (a) 1 L TBPB dosed on SLG/Cu at 200 K, (b) after 260 K annealing, and (c) after 400 K annealing. The absence of any noticeable changes upon surface annealing indicates that no thermal reaction took place.

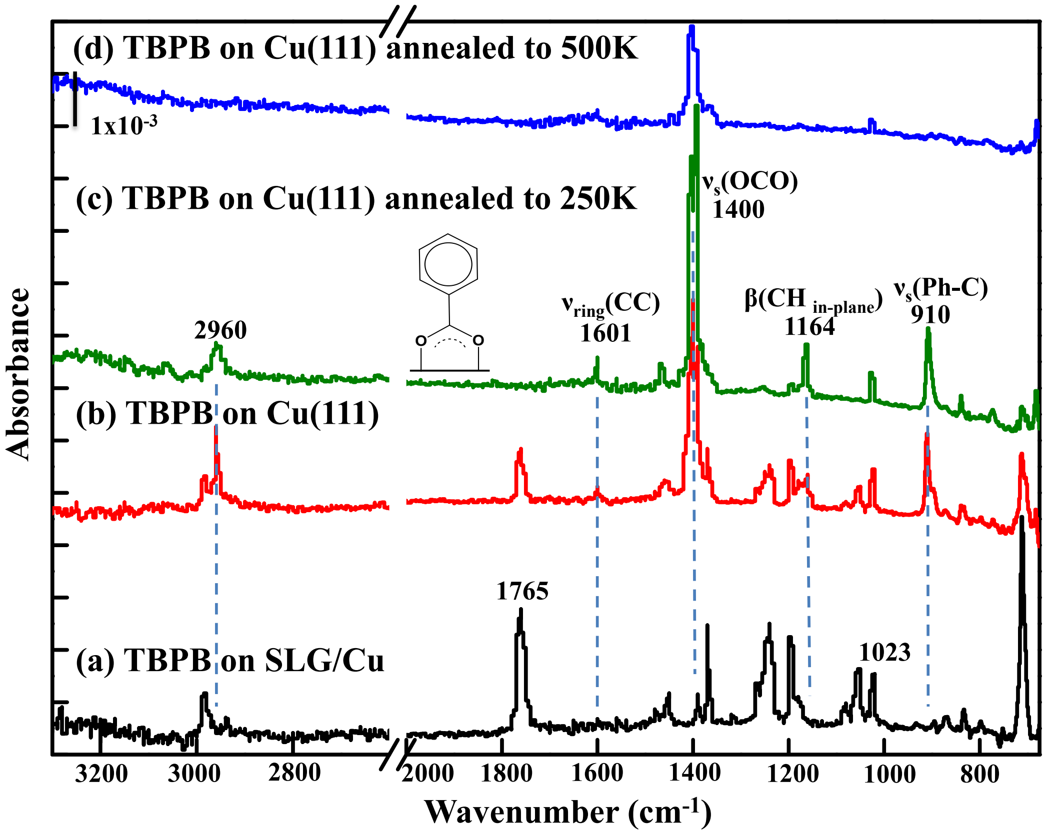

Fig. S3 RAIR spectra of (a) 0.1 L TBPB dosed on SLG/Cu at 200 K, (b) 0.1 L TBPB dosed on Cu(111) at 200 K, (c) sample (b) after 250 K annealing, and (d) sample (b) after 500 K annealing. A portion of TBPB molecules underwent thermal decomposition at 200 K to give new IR bands at 2960, 1601, 1400, 1164, and 910 cm^{-1}. Complete conversion was achieved at 250 K to afford the upright surface-bound benzoate as depicted.

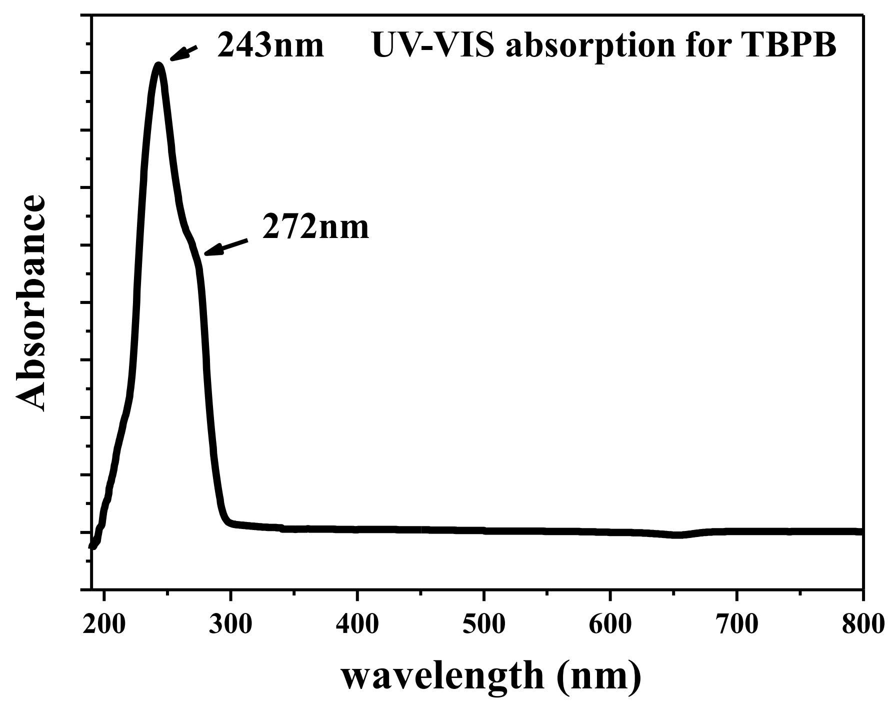

Fig. S4 UV-VIS absorption spectrum TBPB. TBPB is transparent to the 365 nm UV irradiation.