

Supplementary Information

Visualising Structural Modification of Patterned Graphene Nanoribbons using Tip enhanced Raman Spectroscopy

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1. Fabrication of Graphene Nanoribbons

Using natural graphite crystals and mechanical exfoliation method, monolayer graphene flakes were obtained on SiO₂/Si substrate. Monolayer nature of the graphene flakes was confirmed using optical microscopy contrast and Raman spectroscopy. To deposit electron resist layer, a ~150 nm thick film of poly(methyl methacrylate) (PMMA, MicroChem Corp, USA) was spin coated on the graphene flakes and baked at 150 °C for 5 minutes.

Patterning of the spin coated PMMA film on graphene, was performed using electron beam lithography (EBL) system (Zeiss Sigma, Germany) at 20 kV, 10 pA current, 8 mm working distance, 8 nm step size and 200 μC/cm⁻² as area dose. After developing the exposed regions using methyl isobutyl ketone/isopropanol alcohol in 1:3 ratio, graphene was etched in exposed areas using 10 W oxygen plasma for 30 s. Patterned PMMA acted as mask to protect un-exposed area of graphene from plasma etching. The PMMA layer was removed using acetone via gentle ultrasonic treatment. After 30 minutes of dipping in acetone bath, the sample was dried using a nitrogen gun. Using this procedure, graphene nanoribbons (GNRs) with 60 ± 5 nm width, >100 μm length and 140 nm gap were obtained.

GNRs were transferred onto a gold substrate using wet transfer method. Briefly, 200 nm film of PMMA was spin-coated on the GNR sample from a 4% solution in anisole and baked at 130 °C for 2 minutes. As supporting frame, an adhesive tape (Nitto, Japan) with 2 mm hole was placed on the PMMA/GNR region. GNRs were detached from the SiO₂/Si substrate by dipping in 10 % KOH solution for ~3 hours. Then using home-made micro-transfer machine, the GNRs in window tape were transferred onto a Si substrate with 100 nm gold thin film followed by removal of the PMMA film and tape. After short baking at 130 °C, PMMA was washed away using acetone bath. PMMA residues were removed by annealing of the GNRs in Ar/H₂ (5%) atmosphere at 280 °C for 3 hours. The fabricated GNR samples were used for the TERS study without further treatment.

2. TERS measurements

TERS measurements were conducted using a NanoRaman system (HORIBA Scientific, France) in side-reflection mode and gold-coated TERS tips ($k = 2.7$ N/m, $f = 60$ kHz, OMNI, HORIBA Scientific, France). TERS spectra were measured using a spectrometer grating of 600 lines/mm and an electron-multiplying charged-coupled device detector (HORIBA Scientific, France). A 638 nm excitation laser was focused on the sample in side-illumination geometry at an angle of 60° using a 100×, 0.7 NA, 6 mm long working distance objective lens (Mitutoyo, Japan). An intermittent contact AFM feedback

was employed for TERS imaging whereby at each pixel TERS spectrum was measured with the tip in direct contact with the sample and the movement of tip relative to the sample (between pixels of the TERS image) was performed using semicontact AFM feedback. This hybrid contact + semicontact AFM feedback helps preserve the sharpness and plasmonic enhancement of the tip during TERS imaging by eliminating lateral forces that might pick up contaminants from the sample surface. For TERS measurements, laser power at the sample was set to 130 μ W.

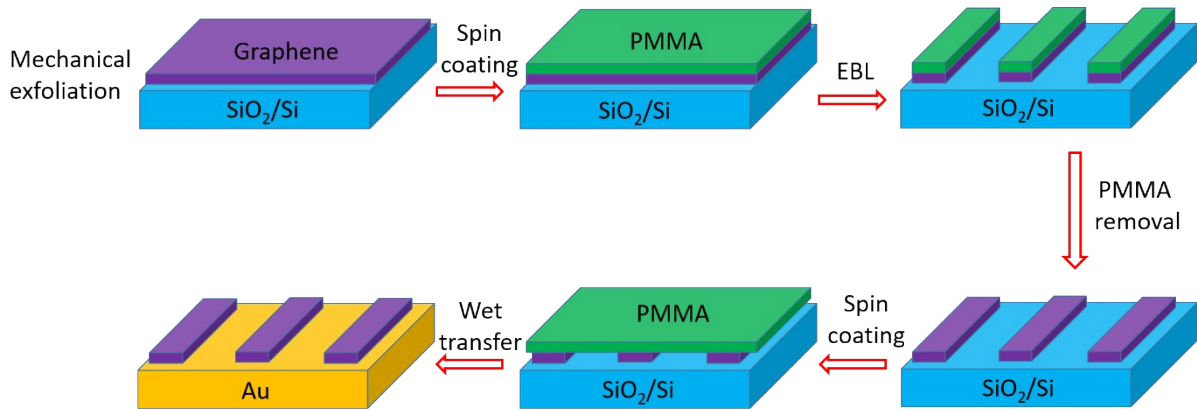


Fig. S1. Schematic diagram illustrating the fabrication process of GNRs.

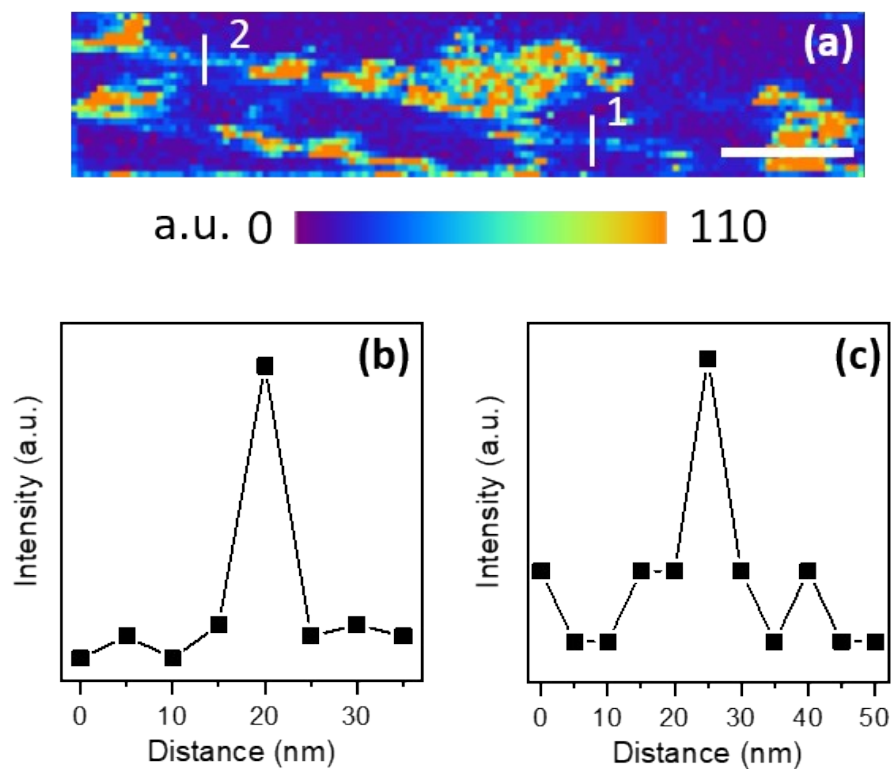


Fig. S2. (a) TERS image of D band intensity shown in Fig. 3b. Scale bar: 100 nm. (b), (c) Intensity profiles along the lines 1 and 2 marked in (a), respectively.

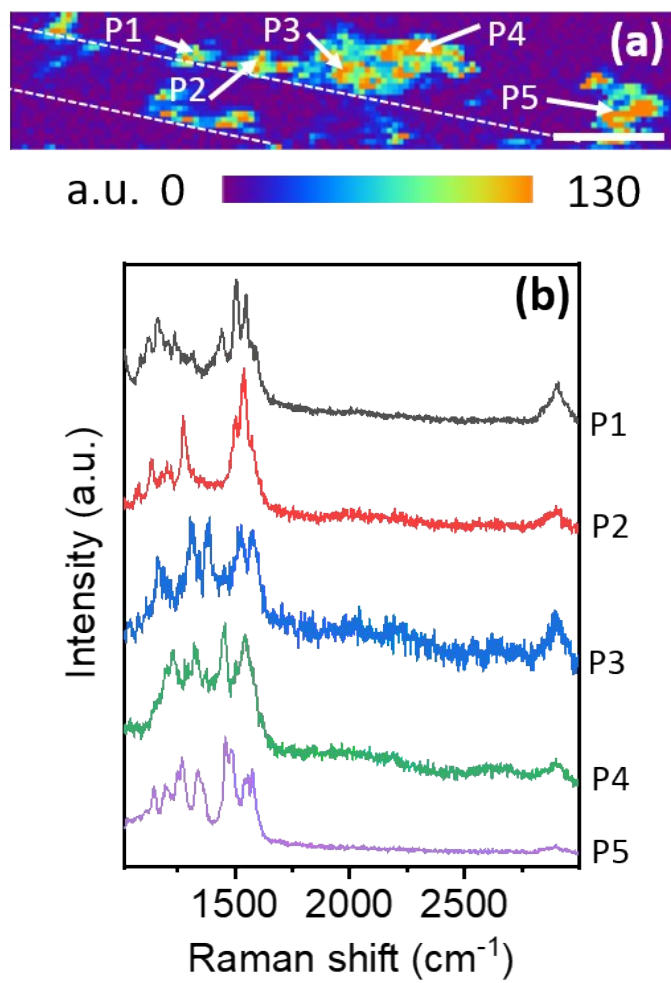


Fig. S3 (a) TERS image of 2890 cm⁻¹ band intensity (b) TERS spectra measured at the locations marked in (a).