Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Characterization of SiC-grown epitaxial graphene microisland using tip-enhanced Raman spectroscopy

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A. Semi-low energy SEM images of other graphene microislands

In the same sample as the main manuscript, there were many microislands created. The majority of the microislands are also hexagonal. Some large graphene islands (with a size of several hundred micrometers) show a complicate shape and contain multiple layers. However these large islands are rare.

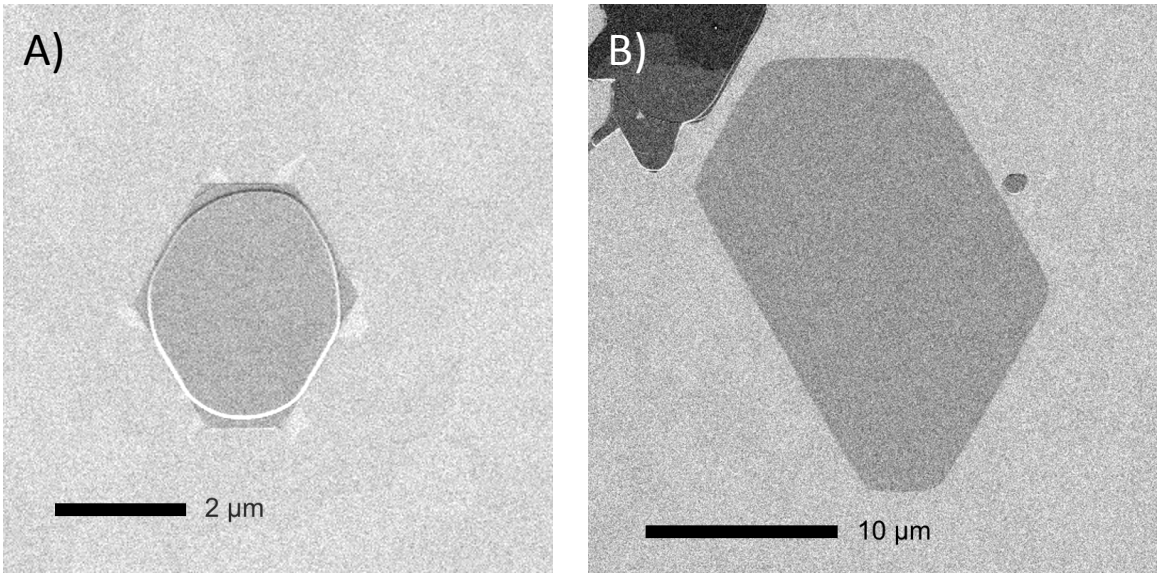

Figure S1. Semi-low energy SEM images of graphene microislands with SiC plateau as the nucleation site.

B. D band map in micro Raman imaging

These D band maps are derived from the same dataset as the maps in Figure 2 of the main manuscript. Since the D band is absence, the peak fitting failed for every spectrum. Therefore these maps were created using area integral instead. As expected, the island does not exhibit significant defect signal. (The integral values on the island are similar to the surrounding SiC, which certainly lacks of graphene defects).

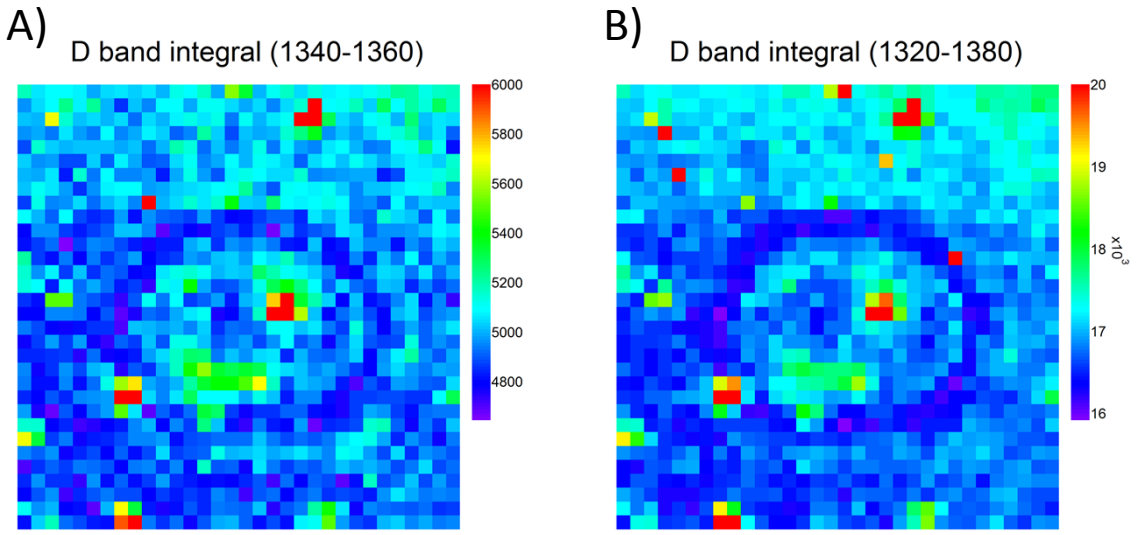

Figure S2. D band mapping generated by area integral of Raman spectra in the range of A) 1340 to 1360 cm^{-1} and B) 1320 to 1380 cm^{-1}.

C. Resolving of the broad G’ band in TERS spectra from nanoridge

As discussed in the main manuscript, a possible explanation of G’ band broadening in TERS spectra is the band splitting due to the uneven strain in different axes. To investigate the splitting, double Lorentzian fitting was applied on the G’ band of each TERS spectra from nanoridges. Figure S3a show the fittings. Due to small splitting, one Lorentzian peak (black peak) is fixed at 2691 cm^{-1} (the average peak position from flat areas). Without the fixing, the fittings do not converge very well.

Figure S3b summarizes the analysis. The lower peak (blue peaks) from point 2 and 3 shows unreasonable FWHM values of around 15 cm^{-1}. This clearly indicates that the very small splitting and the noise of TERS spectra greatly interfere with the fitting. Nevertheless, the G’ band from point 1, with relatively larger splitting, resolved very well into two peaks at 2674 and 2691 cm^{-1}, both with FWHM of around 30 cm^{-1}.

Using the peak positions of the lower peaks in the strain calculation, the strain relaxations (ridge-flat difference) for point 1 to 4 are 3.03×10^{-3}, 1.56×10^{-3}, 2.24×10^{-3}, and 9.49×10^{-4}, respectively. This is interesting because the values are significantly higher than the relaxation values from single Lorentzian analysis in the main manuscript. However, the reliability of the fitting is an issue. TERS spectra with lower noise are needed to confirm this.

The angle between the polarization of Raman excitation and strain direction affects the intensity of each resolved peak.[1] However, the polarization of the near-field enhancement in TERS depends on tip geometry rather than the polarization of incident laser.[2,3] Without the data of the polarization effect from the tip, the relative intensity between the two resolved peaks cannot be directly interpreted into physical nature of the sample. Nevertheless, the polarization affects only intensity of the resolved peaks, but not their peak positions and FWHM.[1] Therefore, this polarization effect does not interfere with the analysis in the previous paragraphs.

All peak fitting was done using the Multi-Peak Fitting 2.0 function of Igor Pro 6.3.

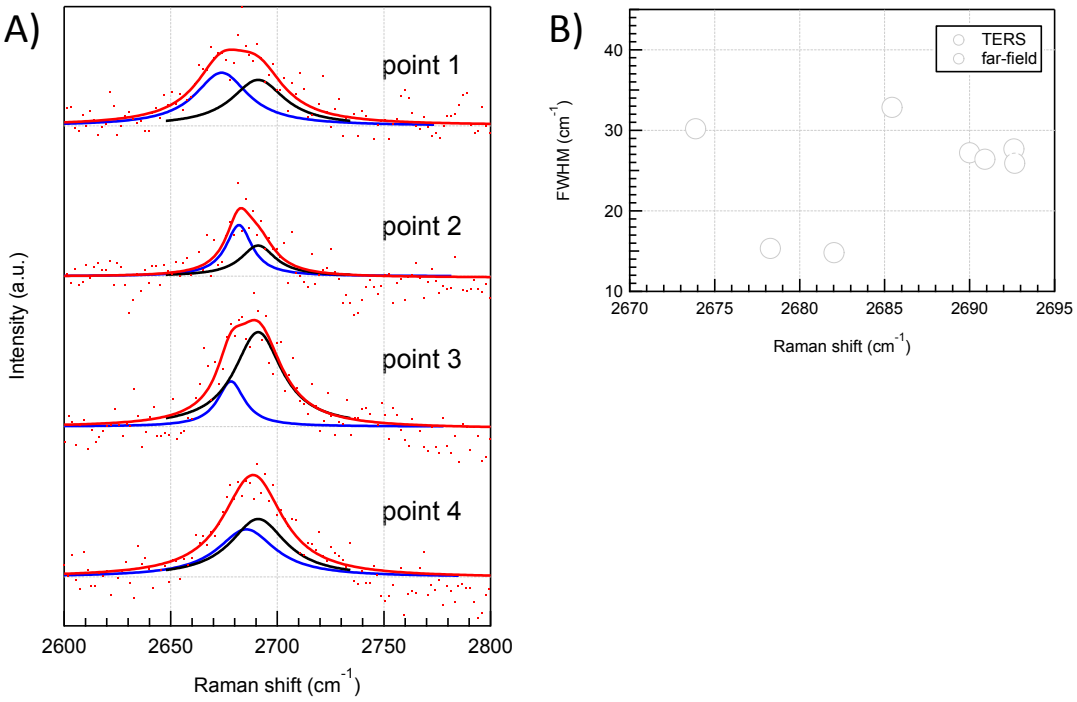

Figure S3. A) Peak resolve of G' band in TERS spectra from nanoridge. Blue and black lines represent the two Lorentzian peaks, with the black peak fixed at 2691 cm^{-1}. The red lines represent the summation of the two peaks. B) A reconstruction of Figure 3a of the main manuscript, using the lower peak of double Lorentzian fitting in A) for TERS result. The data of far-field spectra are unaltered from the original.

D. The absence of D band in TERS spectrum from edge

This is also discussed in the main manuscript.

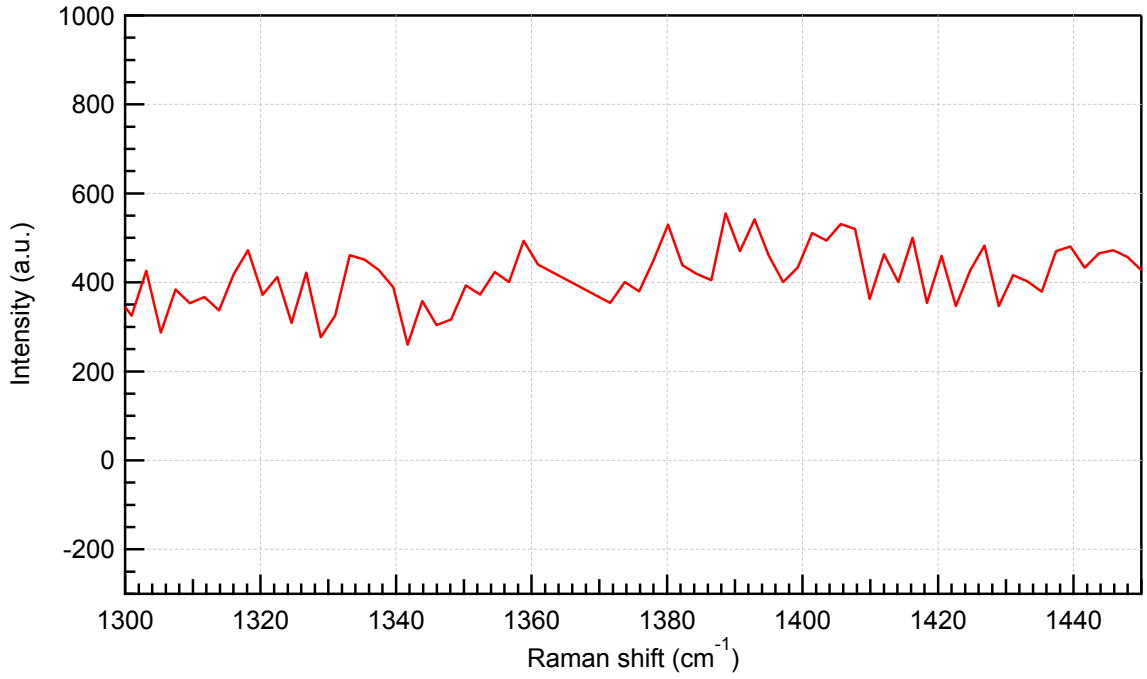

Figure S4. TERS spectra from an edge of graphene microisland showing an absence of D band (~1350 cm^{-1}).

References

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