Supporting Information for the manuscript:

Raman Modes of MoS_2 Used as Fingerprint of Van der Waals Interactions in 2-D Crystals-Based Heterostructures

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1) Calculation of the strain in Gr/MoS_2 heterostructures placed on Si/SiO_2

Strain causes the Raman peaks to change position. This is described by the Gruneisen parameters (γ), which uniquely depend on the material. Therefore, if one knows the Gruneisen parameters of the material and the Raman shift (ω-ω_0, where ω_0 is the initial wavenumber), the (biaxial) strain (ε) can be calculated by: $\varepsilon=(\omega-\omega_0)/2\ \gamma\omega_0$.

In our case, we observed a 2D peak shift of 13-14 cm^{-1} from the position measured on the initial substrate. Since the shift is comparable and graphene should be virtually undoped on MoS_2, then we can assume that also the doping level of graphene on Si/SiO_2 is negligible. Using a shift of 13-14 cm^{-1}, an initial position of 2685 cm^{-1}, and γ_{2D} of 2.6,[1] we obtain a strain of about -0.1% (the negative sign means that graphene is compressed). The strain may be slightly higher for heterostructures where graphene lies directly on Si/SiO_2, in case of doping from charged impurities.[2]

The same approach can be applied to MoS_2. Using the Grüneisen parameter for the E_{2g} band of single layer MoS_2 obtained in Ref. 3 (=0.54),[3] a shift of 1-2 cm^{-1} and an initial position of 385 cm^{-1}, we obtain a strain of about 0.2-0.3% (the positive sign means that the strain is tensile).

2) Additional Raman maps and measurements of nG/mMo and nMo/mG heterostructures on Si/SiO_2

Figure S1 shows additional Raman maps of the difference in frequency between the E^1_{2g} and A_{1g} peaks of MoS_2. This has been used to determine the number of layers for the bare single and few layers MoS_2 on the substrate.

Figure S2 shows a Raman map of FWHM(G). No difference is observed in FWHM(G) of Gr on Si/SiO_2 and Gr on MoS_2.

Figure S3 shows additional measurements on different 1G/1Mo and 1Mo/1G heterostructures placed on Si/SiO_2. We can observe that the blue shifts of A_{1g} and 2D band in the two heterostructures are the same as the results shown in the main text.

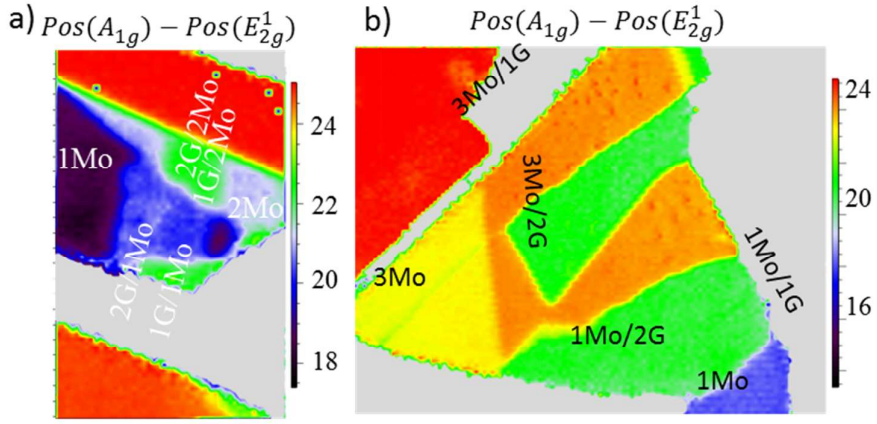

Figure S1 Raman maps showing the difference in frequency of the E^1_{2g} and A_{1g} peaks in: a) nG/mMo and b) nMo/mG heterostructures presented in the main text.

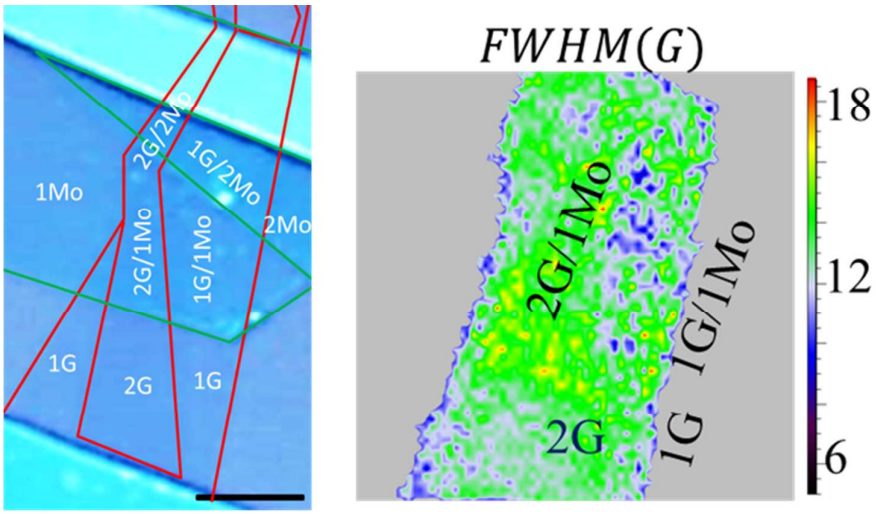

Figure S2 Left: optical image from Figure 1a; Right: Raman map of FWHM of G in nG/mMo (n=1, 2; m= 1) heterostructure.

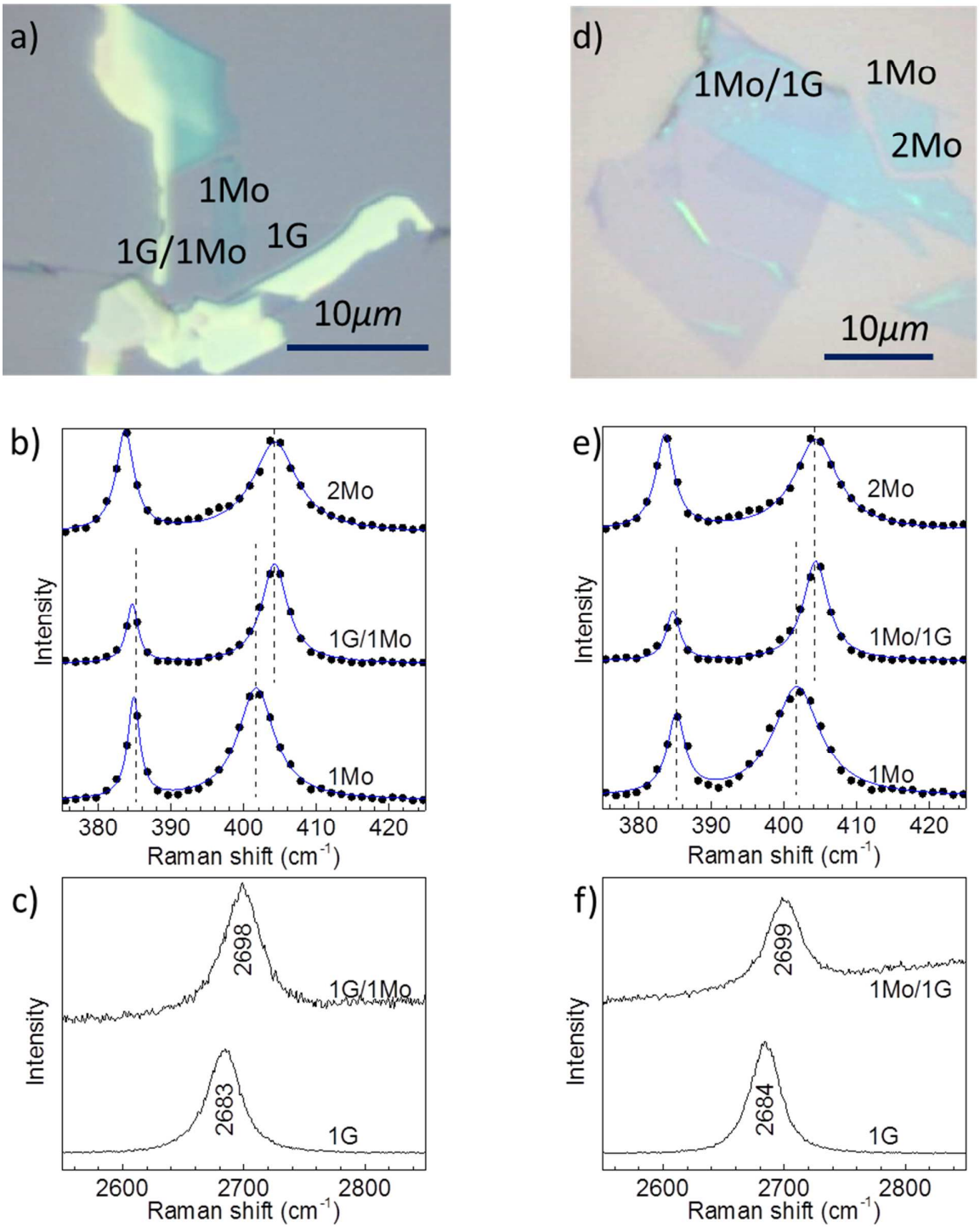

Figure S3 (a) Optical image of nG/mMo heterostructures on Si/SiO_2 (n= 1; m= 1); (b) Raman spectrum of MoS_2 measured for the heterostructures of Graphene/MoS_2 on SiO_2/Si substrate illustrated in (a); (c) 2D- band of graphene measured for different heterostructures. (d) Optical image of additional mMo/nG heterostructures on Si/SiO_2 (n= 1; m= 1); (e) Raman

spectrum of MoS_2 measured for the heterostructures of MoS_2/Graphene on SiO_2/Si substrate illustrated in (d); (f) 2D- band of graphene measured for different heterostructures.

3) Raman study on WS_2/graphene heterostructure placed on Si/SiO_2

We also studied a heterostructure composed by WS_2 (W) and graphene (1W/1G) placed on Si/SiO_2, Figure S4. We obtained similar results for 1Mo/1G heterostructures placed on Si/SiO_2, i.e. we observed that the position of the A_{1g} mode of 1W/1G was located at 419 cm^{-1}, which is 1 cm^{-1} higher than the 1W (418 cm^{-1}), similar to 2W (419 cm^{-1}) (Figure S4 b and c).

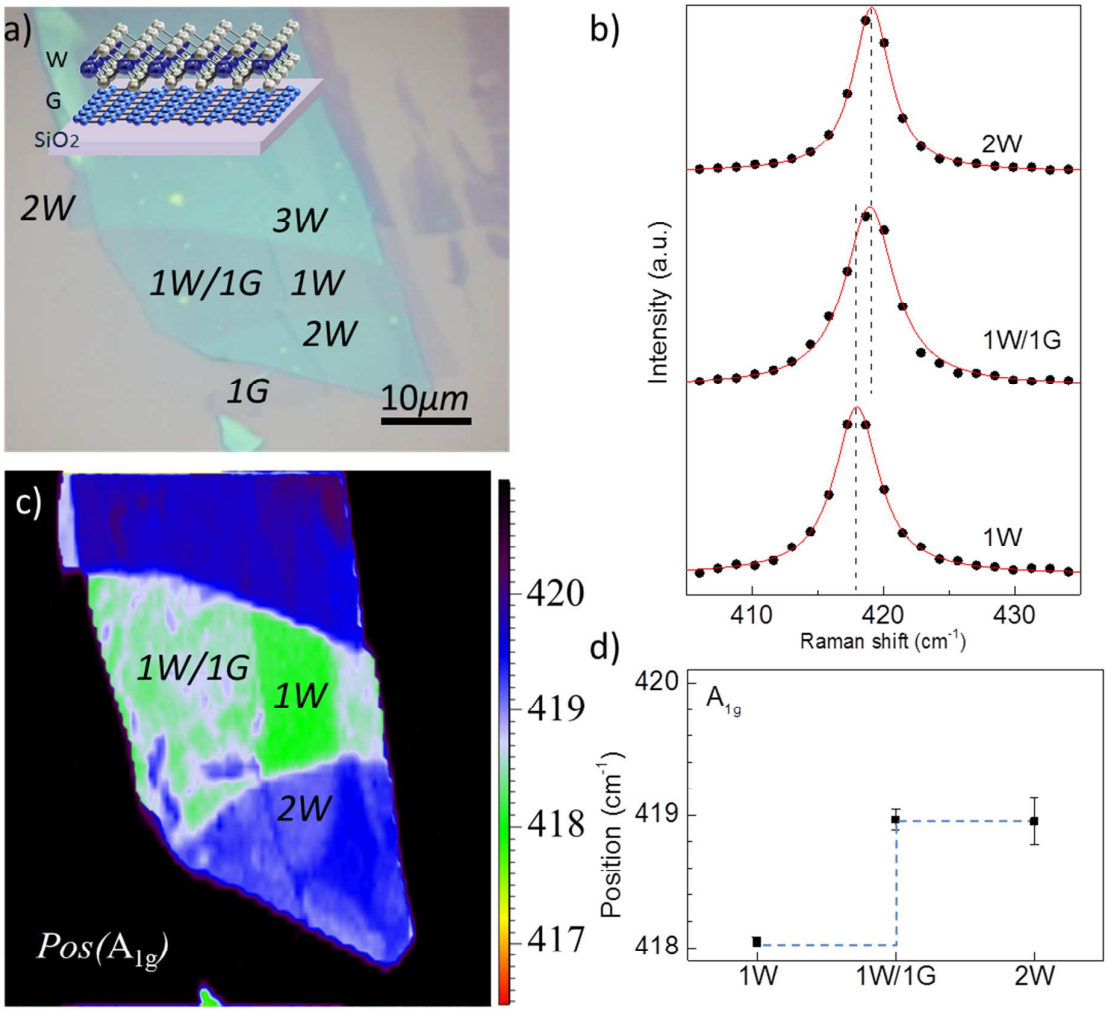

Figure S4 (a) Optical image of nW/mG (n=1, 2; m=0,1) heterostructure; (b) A_{1g} Raman peaks for bare single and bilayer WS_2 and its heterostructure.(c) Raman map of A_{1g} position; (d) A_{1g} peak positions extracted from the spectra in (b) by fitting the peaks with a Lorentzian lineshape.

4) Raman measurements on suspended Gr/MoS_2 heterostructures

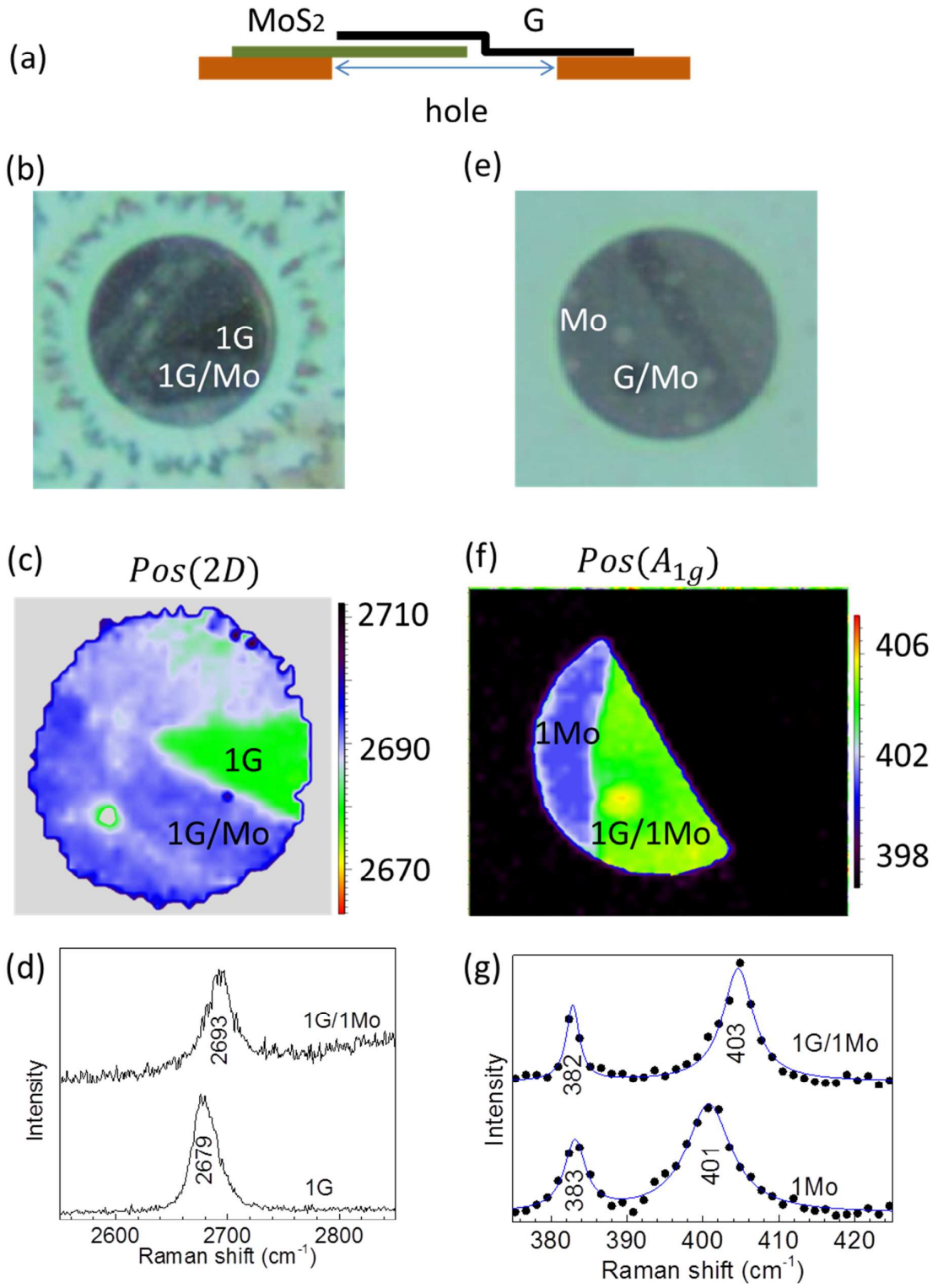

Figure S5 (a) Schematic of suspended graphene/MoS_2 heterostructure; (b) Optical image of suspended nG/mMo (n=1; m=1) heterostructure; (c) Raman maps of the 2D peak position of the heterostructure in b; (d) 2D peaks of suspended bare graphene and graphene/MoS_2

heterostructures in b; (e) Optical image of suspended nG/mMo (n=1; m=1) heterostructure; (f) Raman map of A_{1g} peak position of hetero structure in e; (g) A_{1g} peaks of suspended bare MoS_2 and graphene/MoS_2 heterostructures in e.

In order to investigate the effect of the substrate, we also studied some suspended heterostructures (Fig. S5a). Those have been fabricated following the procedure described in Ref. 4.[4] The heterostructure are loaded over a pinhole with 10 μm diameter. Graphene is only partially covered by MoS_2 (Fig. S5b), so we can directly compare the Raman spectra taken on the heterostructure and on the bare graphene. Figure S5c shows the Raman map of the suspended graphene/MoS_2 heterostructure. The green region (2679cm^{-1}) corresponds to the suspended monolayer graphene, and light blue region (2693cm^{-1}) corresponds to the suspended 1G/1Mo heterostructure, indicating that the position of 2D band for heterostructure has a blue shift of +14 cm^{-1} compared to the bare graphene (Fig. S5d), which is similar to the results in Fig. 1(h). We fabricated a second heterostructure, where this time graphene was partially overlapping MoS_2 (Fig. S5e). In this case we observe that the A_{1g} peak of monolayer MoS_2 shows a blue shift in the suspended heterostructure compared to its bare reference (Fig. S5f). As we can find similar blue shifts of 2D band and A_{1g} peak in the suspended heterostructure (Fig. S5g), compared to the structure in Fig. 1, we can exclude any effect from the substrate in the shift of the peaks observed in the nG/mMo heterostructures on Si/SiO_2.

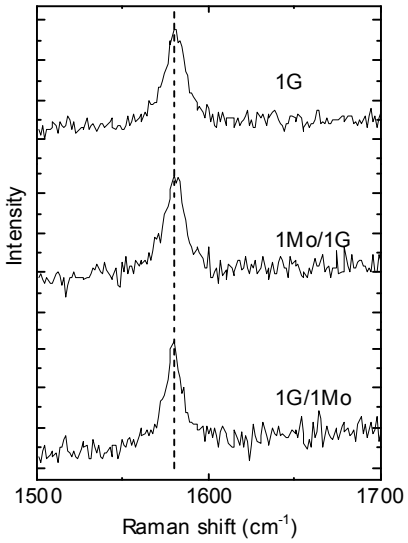

Figure S6 G band of suspended graphene, 1Mo/1G and 1G/1Mo heterostructures.

It is also interesting to look at the G peak position in those heterostructures. We found in supported heterostructures that the G band does not shift when graphene is placed on top of MoS_2, but the peak shifts of 5 cm^{-1} when graphene is encapsulated between the substrate and MoS_2 (fig 4). If we look at our suspended heterostructures, we observe no difference in the G peak position of the suspended heterostructures 1G/1Mo and 1Mo/1G, compared to free standing graphene, Figure S6. From those results, we conclude that the shift in G position is fingerprint of the encapsulated graphene, although its origin is still under discussion. [5-6]

5) Other out-of-plane phonons to probe the interfacial contact

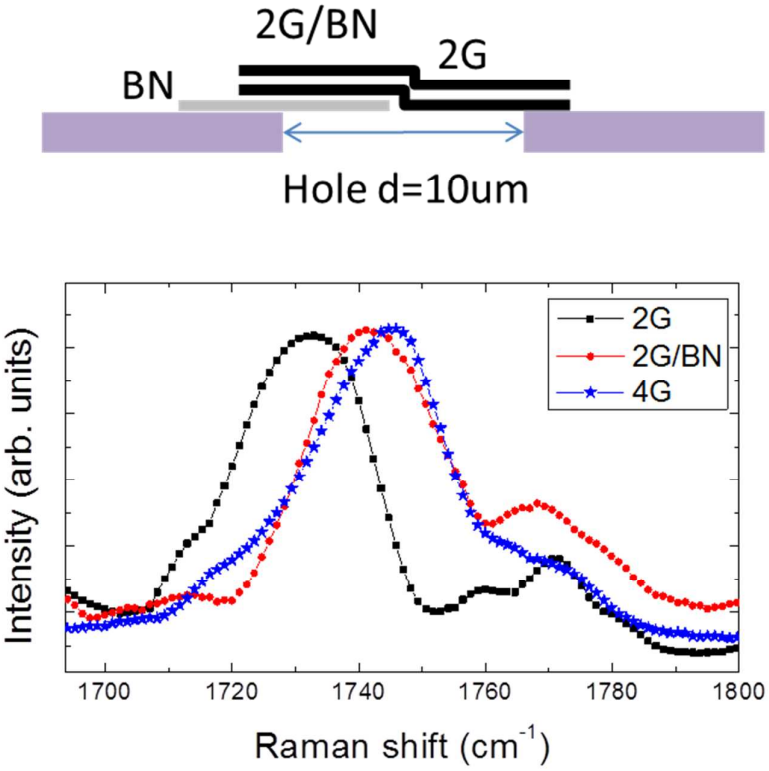

Figure S7 The out-of-plane Raman phonons in a suspended graphene/BN heterostructure as compared to bilayer (2G) and 4-layers graphene (4G).

Similar to the A_{1g} peak of MoS_2, other out-of-plane phonons can also act as the probe of the VdW contact. We measured a suspended bilayer graphene/BN heterostructure. Because of the difficulties in measuring low energy modes, we measured the out-of-plane Raman signal (LO+ZO'), which is placed between 1720-1750 cm^{-1}, depending on the number of layers.[7] We find that the LO+ZO' signal of bilayer graphene/BN heterostructure is hardening up getting closer to 3-4 layers graphene,[5] which is similar to the results obtained for the A_{1g}

mode of MoS_2 shown in the main text. However, we expect it to be more difficult to extract accurate information on the quality of the contact from those peaks because their exact position is also affected by the stacking of the layers.[7]

6) Raman study of BN/1G/MoS_2 heterostructures characterized by different mobility

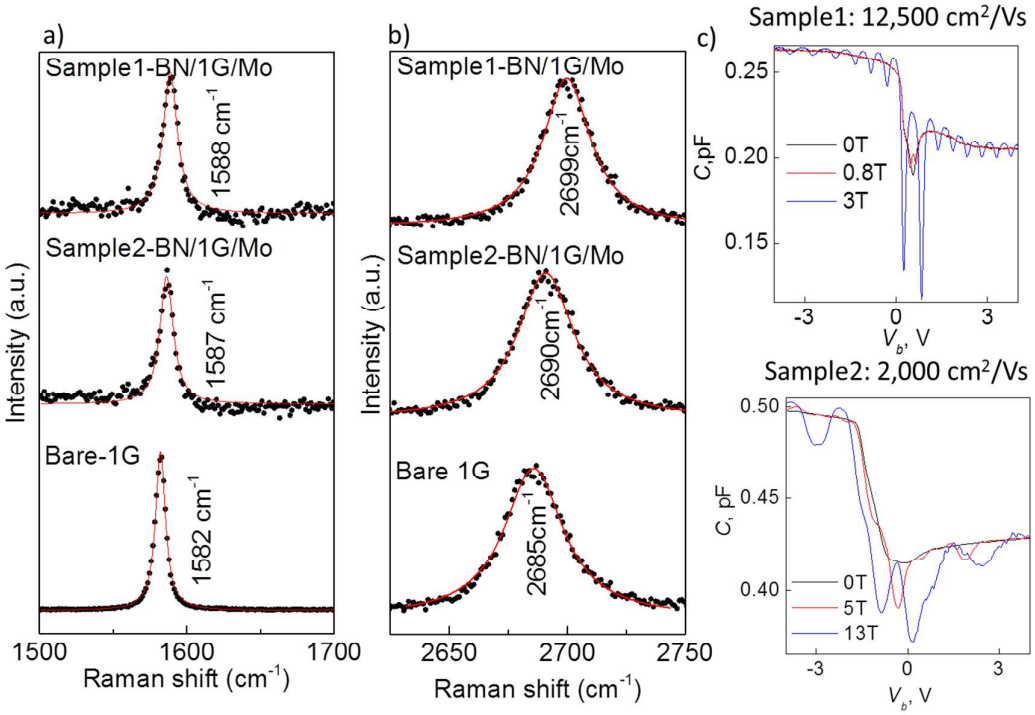

Figure S8 G (a) and 2D (b) band of bare graphene and BN/1G/MoS_2 heterostructures (sample 1 and sample 2). (c) capacitance measurements[6] of the two devices, showing that they have different mobility.

We applied our results to heterostructures (called sample 1 and 2) previously measured by transport measurements. Details of the fabrication and characterization of those devices are presented in Ref 6.[8] In this case the heterostructure is composed by graphene encapsulated between hexagonal Boron Nitride (BN) and MoS_2 thin flakes. Since the MoS_2 is not a single-layer, we focus on the 2D peak shift. Figure S8 compares the 2D peak position in bare graphene, and in the heterostructures. One can see that the 2D position of sample 1 is hardened by +14 cm^{-1}, which is similar to that found in Figure 1 for the heterostructure with high quality contact between the crystals. In contrast, the 2D band in sample 2 is only shifted by +5 cm^{-1}. This should correspond to a bad quality contact between the crystals. Transport

measurements are in agreement with our conclusions since sample 1 has mobility about 6 times higher than sample 2. This is attributed to the better contact between the crystals.

7) Changing the interfacial contact by Atomic Force Microscopy

Unlike chemical vapour deposition technique, the dry transfer process[9] relies on the Van der Waals (VdW) interaction between layers. Theoretically it has been shown that the VdW interaction is too weak (and so disappears) when the interlayer distance is over 4 nm.[10] Therefore, if a substrate is too rough (i.e. average roughness above 4 nm), the quality of the interface can be strongly affected.

In the case of our heterostructures on mica, we have to take into account that some area of MoS_2 will be suspended between the different terraces of the mica substrates (the substrate is not flat, but show area of different heights). As a consequence, the contact at the suspended region does not exist and form a "pseudo-soldering" region. Our method to repair the "pseudo-soldering" is to apply a gentle force on the top layer by using the tapping mode of an atomic force microscope (Multidimension AFM by Veeco). A setpoint of 362.69 mV (~220nN) was applied to the tip to compress the top layer. The scanning rate was set to 15μm/s. As shown in Fig. 6, the interfacial contact was found to be improved after treatment by AFM.

References

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