

Supporting Information

Enhanced Photoluminescence of Solution Exfoliated Transition Metal Dichalcogenides *via* Laser Etching

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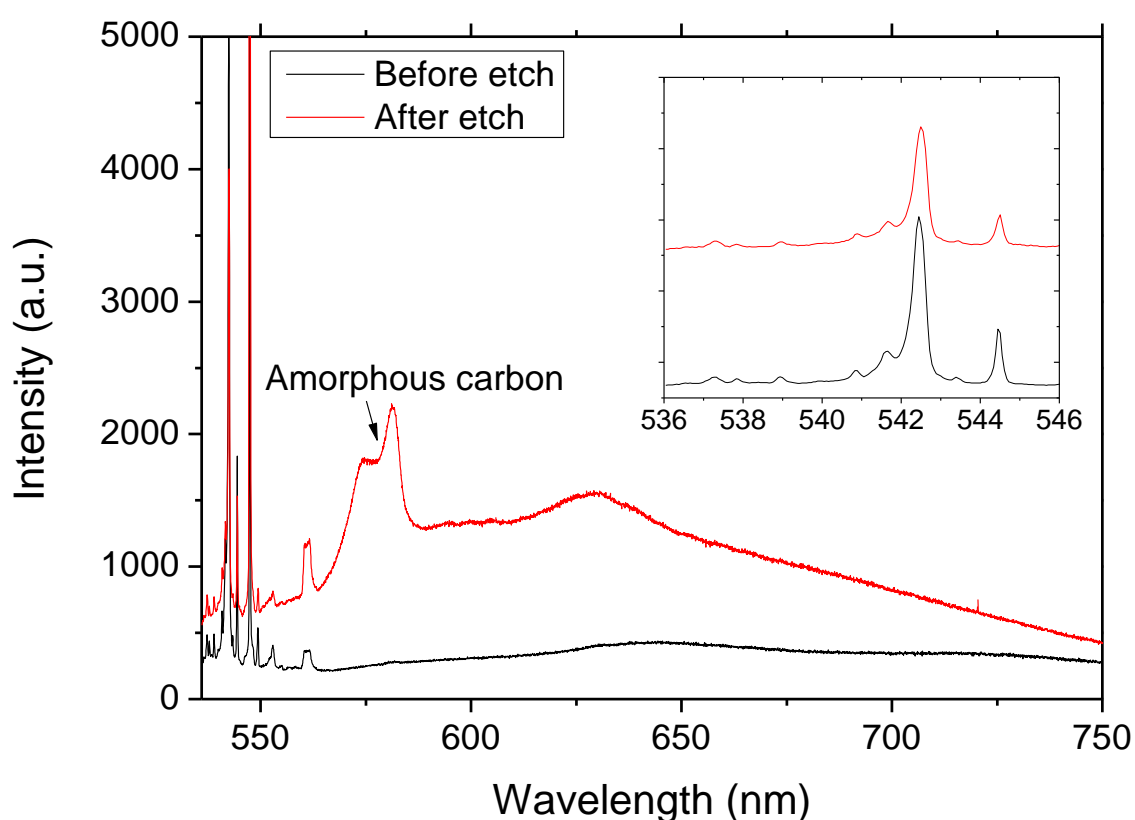


Figure S1. Plot comparing the photoluminescence spectra of the as deposited WS₂ flakes before (black) and after (red) laser etching without the additional vacuum annealing procedure. Clearly, without the additional cleaning step there is a large amorphous carbon peak after the laser etching procedure. Although the PL response of the WS₂ is increased compared to the as deposited, it is significantly quenched by the amorphous carbon compared to the vacuum annealed spectra shown in Figure 2 of the main text.

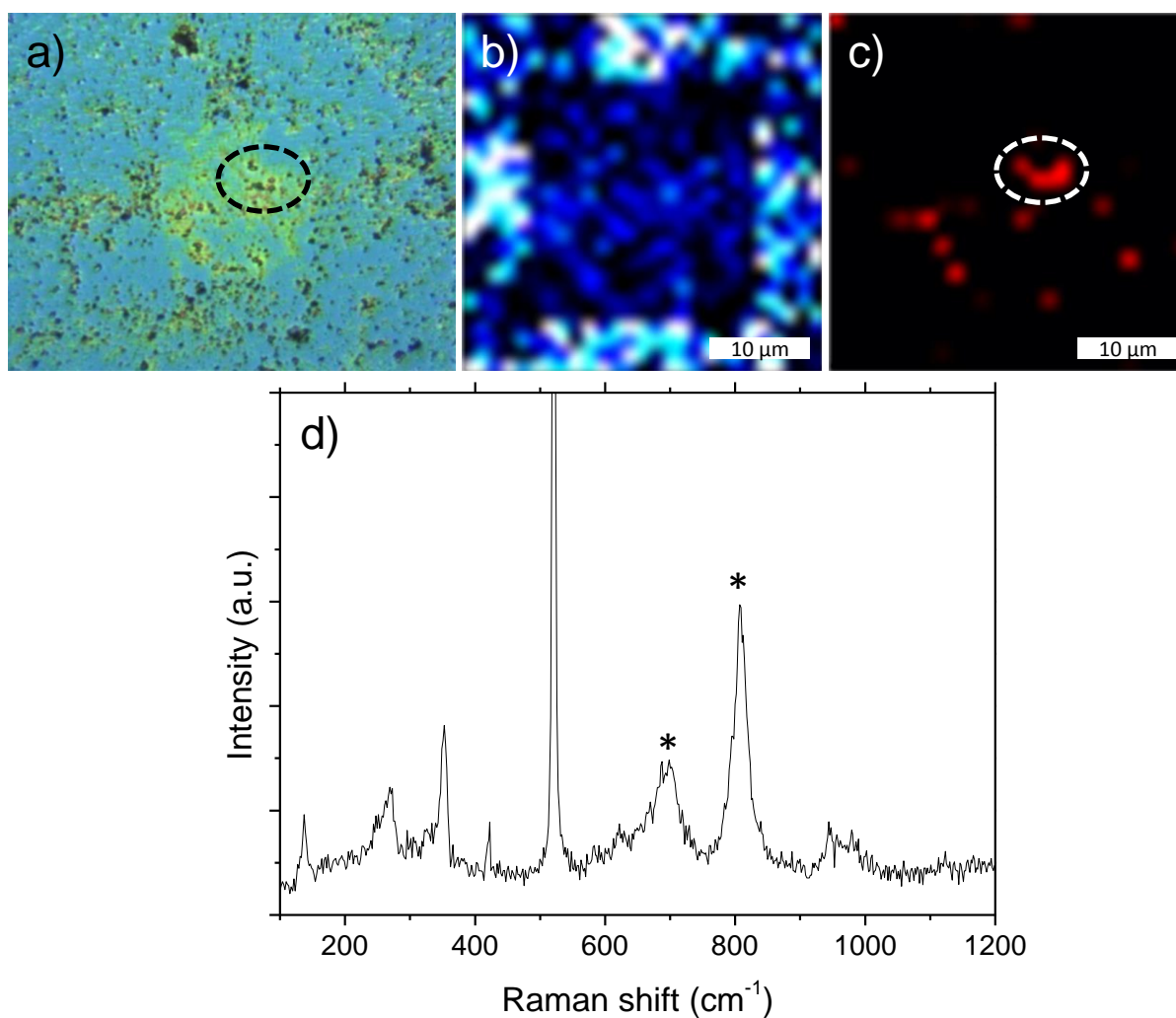


Figure S2. a) Optical image of exfoliated WS₂ flakes deposited on Si/SiO₂ wafer after laser etching. b) Raman map of WS₂ E_{2g} intensity over laser etched area. c) Raman map of WO₃ peak (809cm⁻¹) intensity. It can be seen that oxide peaks occur rarely and are only associated with the thickest areas of flakes. d) Raman spectrum of circled area shown in (a, c) showing clear Raman peaks associated with WO₃.

AFM Analysis

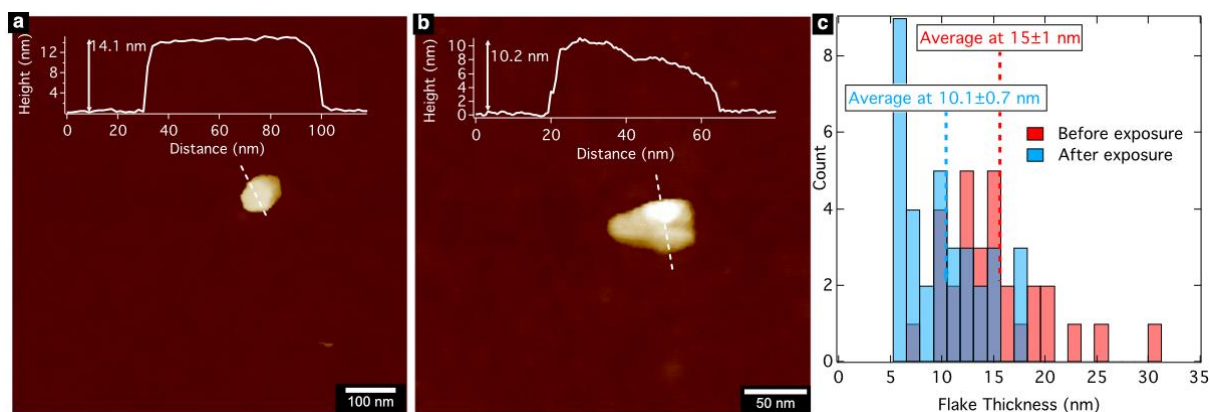


Figure S3. AFM of WS₂ deposited on SiO₂ before (a) and after (b) laser etching. These measurements were repeated across both pristine and laser-exposed regions, and a histogram of the thickness measurements is presented in (c).

Figure S3a is an AFM image of an exfoliated WS₂ flake after deposition onto SiO₂ before laser etching, and S3b of the same sample (but in a different region) after laser etching. Both images show a single flake 50-100 nm across on the flat SiO₂ surface, which are consistent with dimensions expected for flakes of WS₂ produced by sonication. The thickness of these flakes is measured using a line profile across them. These thickness measurements are repeated across many flakes before and after exposure to the laser etching, and the results are displayed as a histogram in Figure S3c. The average measured thickness after laser exposure was 10.1±0.7 nm compared to 15±1 nm before laser exposure. This thickness decrease is consistent with earlier results demonstrating that the laser etching process reduces the thickness of the TMD flakes. Based on the previous work of Coleman *et al.* measuring the thickness of solution exfoliated TMDs with small lateral diameter¹ the thickness of WS₂ should be approximately 1.9 nm / layer. This is in agreement with the measured step height observed within terraced flakes in our work.

Before etching the WS₂ flakes had an average height of 15nm (7-8 layers), this is larger than that determined from the Raman (2-3 layers) likely due to some restacking combined with AFM tip interactions making accurate thickness measurements for very small flakes difficult.² After a single cycle of laser etching the thickness decreases to an average of 10nm (5-6 layers), with the majority of flakes having a thickness of ~5 nm (2-3 layers), and this closely matches the increased PL response we see in Figure 2 of the main text. With subsequent etching cycles we can begin to increase the number of monolayer flakes present in the coating, and thus increase the PL intensity.

MoS₂-WS₂ heterostructures

Figure S4a shows the absorption spectra for the exfoliated and centrifuged dispersions of both MoS₂ and WS₂ in NMP. As expected in the MoS₂ dispersion (black) we observe two excitonic absorptions, labeled A (1.85 eV) and B (2.05 eV) while for WS₂ (red) we also see both the expected A (1.95 eV) and B (2.35 eV) excitonic absorptions. By mixing the dispersions of each materials in a 1:1 (wt%) ratio, and briefly sonicating to ensure a homogenous distribution, we can create a mixed heterostructure dispersion. By removing the scattering background seen in the absorbance spectrum we can also more easily detect any changes in the heterostructure solution, as seen in Figure S4b. In Figure S4b we can also more easily see the individual excitonic absorptions for the MoS₂ and WS₂, as well as the differences in the relative intensity of the A and B transitions. The absorption spectrum of the combined dispersion is also shown, and exists as an overlap of each of the individual absorbance components with no noticeable shifts in absorbance energy or relative intensity, as expected.

These mixed dispersions can then be deposited onto a substrate, and with the removal of the solvent, spontaneously form MoS₂-WS₂ heterostructures. The Raman spectrum of these spontaneously formed heterostructures is shown in Figure S4c. Both of the respective signature Raman components can be detected and are labeled with Lorentzian fits in red (MoS₂) and blue (WS₂) indicating that indeed both materials have formed a closely stacked structure. All of the flake stacks analyzed contained Raman signals unique to both materials, indicating that during the mixing of the dispersion and subsequent deposition onto the surface both materials were homogeneously distributed.

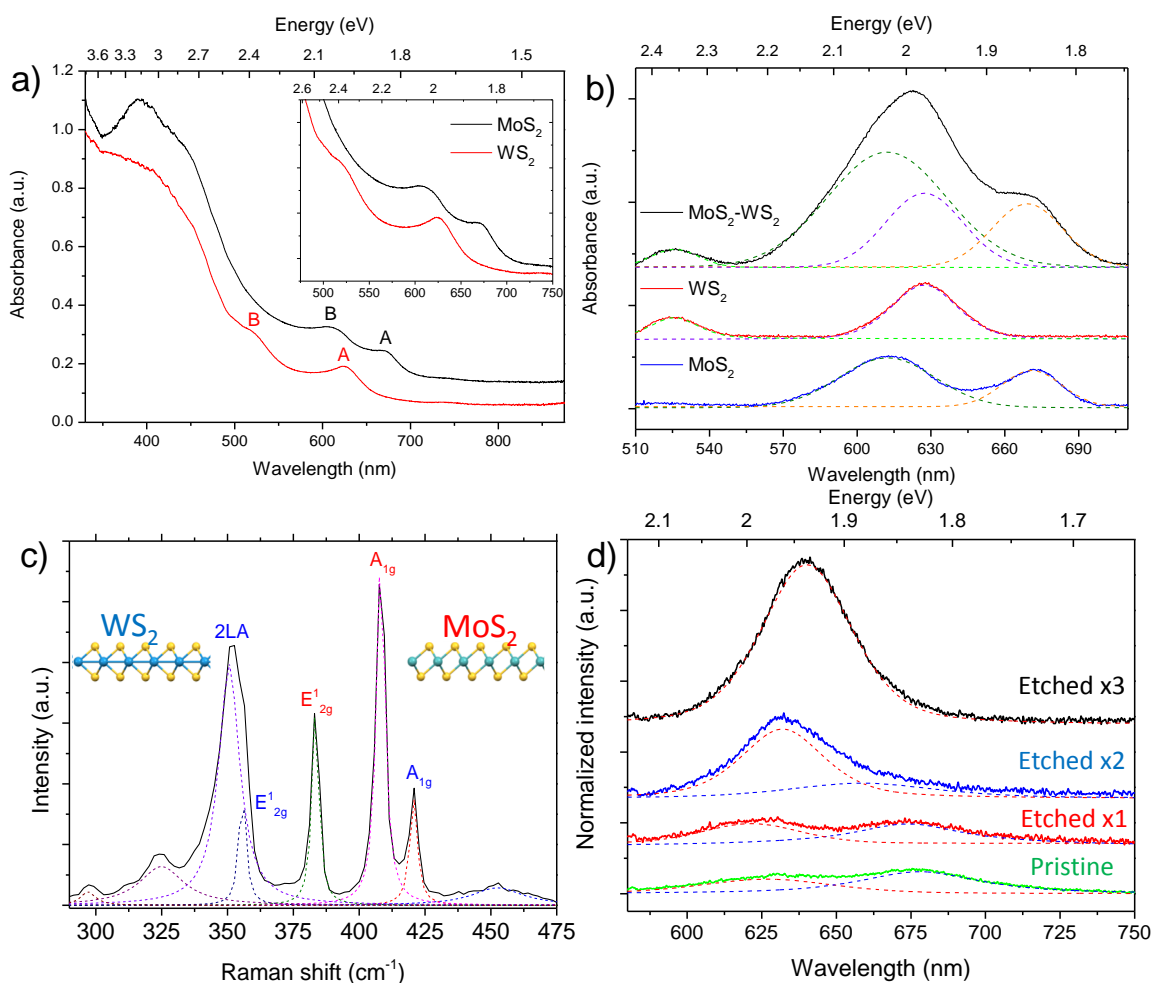


Figure S4. (a) Absorbance spectra for the exfoliated and centrifuged MoS₂ and WS₂ dispersions in NMP. (b) Scattering background subtracted spectra for each of the individual (MoS₂ and WS₂) dispersions along with the combined (1:1 wt%) dispersion. (c) Representative Raman spectrum of the heterostructure after deposition onto a SiO₂ wafer showing combined Raman features. (d) PL spectra of the heterostructure stack, fitted with Lorentzian components, for the deposited and sequentially laser etched heterostructure. The peak intensity has been normalized to the intensity of the MoS₂ Raman A_{1g} peak.

The PL spectrum of the as deposited heterostructure, after vacuum annealing to remove residual solvent, is shown in green in Figure S4d. It consists of two emission peaks of low intensity, likely due to the thickness of the heterostructure stack. The two components of the PL spectrum of the as-deposited heterostructure are centered at 676 nm (1.83 eV) and 622 nm (1.99 eV) similar to the PL spectrum of the ‘pure’ MoS₂, indicating that the uppermost layer is likely MoS₂. Interestingly the Raman spectrum shows an approximate 1:1 ratio in Raman peak intensity; however the PL intensity appears to be predominantly MoS₂. This indicates that, although the heterostructure clearly consists of layers of both materials, upon

excitation charge transfer between the materials must occur quenching the PL of the lower layers and making only the uppermost MoS₂ detectable. By using the laser etching process we can begin to remove the uppermost layers and effectively ‘depth-profile’ the structure by monitoring the change to the PL and Raman spectra.

The PL spectra after repeated laser etching are also shown in Figure S4d, clearly there is an increase in PL intensity as seen in the main text indicating that the flakes are being thinned and likely doped. The most noticeable difference with the repeated laser etching cycles is a significant shift in the position of the central peak. After the first cycle (shown in red) the peaks increase in intensity but shift by only ~2 nm. However, after the second laser etching cycle (blue) the spectrum changes significantly now consisting of a much more intense peak centered at 631 nm (1.96 eV) and a much lower intensity shoulder at 659 nm (1.88 eV), matching the most intense A exciton transitions of the WS₂ and MoS₂ respectively. This likely indicates a transition point in the layered structure caused by the removal of the MoS₂ layers on top and exposing the thin WS₂ layers. With further etching the PL response can be fitted with a single peak, located at 639 nm (1.94 eV) matching the expected PL response of ‘pure’ WS₂.

This can also be seen when comparing the relative intensities of the corresponding Raman peaks of each of the materials, as seen in Figure S5. By plotting the intensity ratio of the MoS₂ (A_{1g}) and the WS₂ (2LA) we see that initially the signal from the MoS₂ is much larger than the WS₂, indicating the uppermost layers are indeed predominantly MoS₂, in agreement with the PL response. After the first cycle of etching the amount of MoS₂ signal decreases significantly, and with further etching the WS₂ signal intensity increases. From both the Raman and PL response recorded after successive laser etching cycles we can say that the as-deposited heterostructure consists of several layers (2-3) of MoS₂ on top of several (2-3) WS₂ layers.

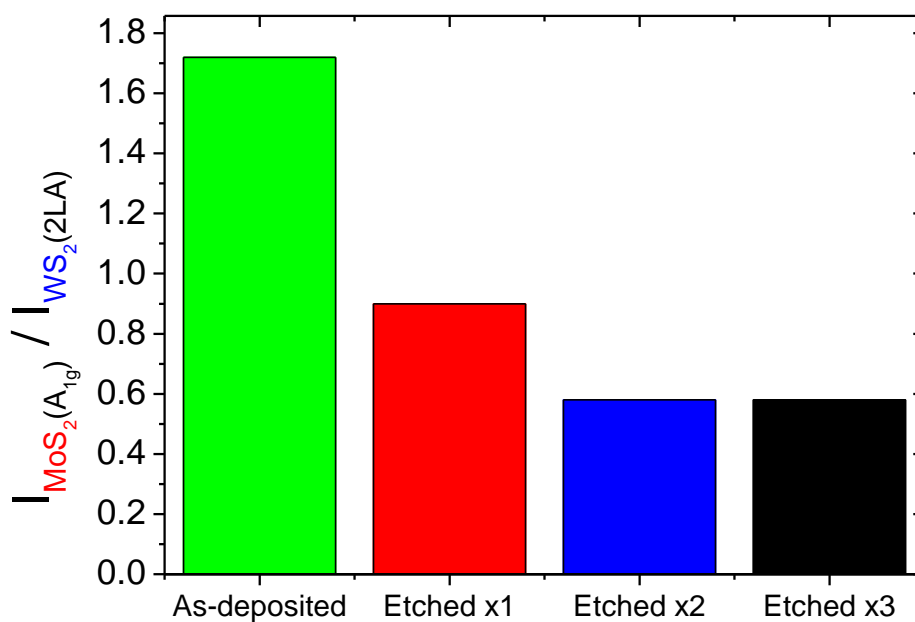


Figure S5. Plot comparing the relative intensity of the MoS₂ (A_{1g}) and WS₂ (2LA) Raman peaks from the heterostructure data shown in Figure 4d of the main text.

Supporting References

1. Backes, C., et al., Edge and Confinement Effects Allow in Situ Measurement of Size and Thickness of Liquid-Exfoliated Nanosheets. *Nat. Commun.* **2014**, *5*, 4576.
2. Shearer, C. J.; Slattery, A. D.; Stapleton, A. J.; Shapter, J. G.; Gibson, C. T., Accurate Thickness Measurement of Graphene. *Nanotechnology* **2016**, *27*, 125704.