Supporting Information.

Comparable Enhancement of TERS Signals from WSe_2 on Chromium and Gold

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Estimation of the far field signal contribution in TERS maps of the WSe_2 crystals exfoliated to gold and chromium can be done by comparing Raman spectra averaged over adjacent (about 100 nm apart) areas along the edge of a WSe_2 crystal and corresponding substrate. With 638 nm excitation wavelength and the numerical aperture of the objective of 0.7, we can estimate the size of the focused Raman laser in our experiments to be about 600 nm, therefore, the signal collected over the area on bare gold adjacent to the edge of WSe_2 crystal can be considered of pure far field nature. Based on the results showed in Figure S1 we can conclude that in case of WSe_2 on gold, the far field portion was about 10-12% of the overall signal, and it was even less than that, about 5-6 % in case of WSe_2 crystal exfoliated to chromium even if we consider the signal from the core of the crystal, this number would go down to 1-2 % if we used TERS signal coming from the edge pixels as the reference.

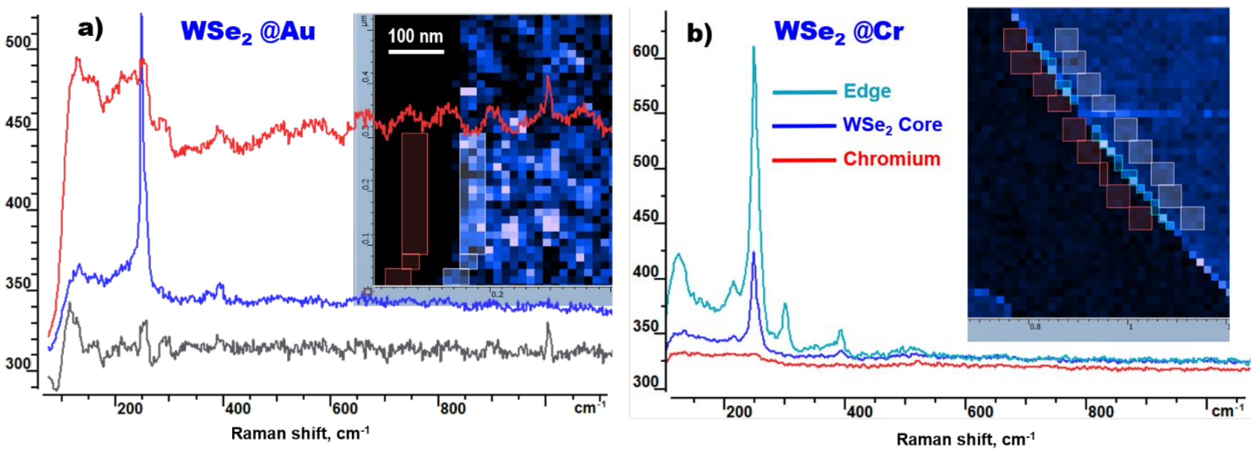

Figure S1. a) WSe_2 on gold. Raman spectra averaged over similar areas along the edge of WSe_2 crystal (blue) and over bare gold (red). Black spectrum is the signal from bare gold with the slowly changing background subtracted. In the insert- a partial screenshot showing the sampling boxes for corresponding spectra; b) WSe_2 on chromium. Raman spectra averaged over similar areas along the edge of WSe_2 crystal (blue), over the edge pixels (dark cyan) and over bare chromium (red). In the insert- partial screenshot showing the correspondingly colored sampling boxes.

In order to understand how the measured thickness of WSe_2 crystals affects the intensity of the TERS response, we ran a set of measurements over crystals of varying height that were exfoliated to gold following the procedure described in the work of Velicky et.al.[S1]. Topography images with corresponding sections are presented in Fig S1 a)-d). The graph showing the TERS signal intensity normalized by the signal from the monolayer as a function of measured height is showed in Fig.S1, e).

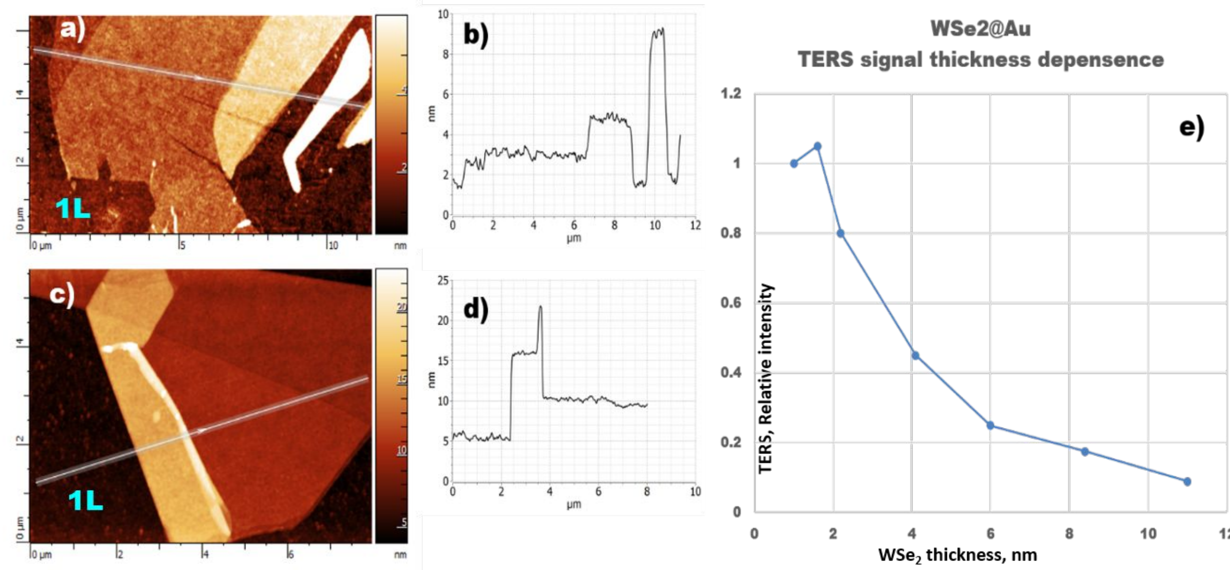

Figure S2. a) Topography and b) section analysis of WSe_2 crystal with the thickness up to about 8nm; c) topography and d) section analysis of the area of the crystal with WSe_2 thickness coming up to about 11 nm; e) relative intensity (normalized by the TERS signal from the monolayer) of TERS signal as the function of thickness, TERS data were obtained with the same TERS probe. Thickness of the first monolayer on gold was assumed to be 1 nm.

Based on this graph, we can compare relative intensities of TERS signal for the 5 and 6 nm thick crystals, which correspond to 0.35 and 0.25 of the intensity of the monolayer correspondingly. Therefore, the thickness-adjusted intensity of TERS signal of WSe_2 crystals on chromium showed in Fig.2 of main text is about 70% of corresponding signal on gold.

In order to confirm the reproducibility of the results obtained in the first round of measurements, new samples were prepared on gold and chromium. This time we have not been able to find the crystals of close thickness and had to compare TERS signal intensity from 4 nm thick crystals on gold versus 8 nm thick crystals on chromium, the thinnest we were able to find (Fig.S2), this time the TERS signal intensity of thicker crystals on chromium was about 4.7 times lower compared to gold, but comparing the thickness-adjusted signals, intensity of the TERS signal on chromium was about 50% of that on gold, which is reasonably close to the results obtained in the first round of measurements.

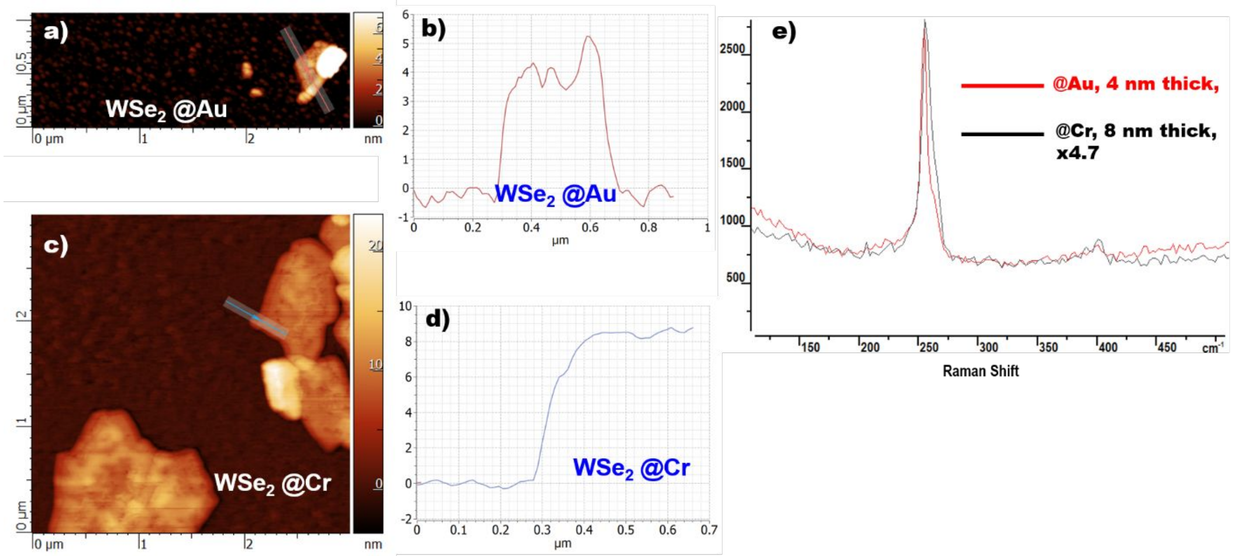

Figure S3. a) Topography image of a thin WSe_2 crystal on gold; b) corresponding section analysis showing that the height of the crystal was about 4 nm; c) topography image of WSe_2 crystals exfoliated to chromium; d) corresponding section analysis showing that averaged height of the crystal was about 8 nm; e) averaged TERS spectra of the crystals on gold (red spectrum) and chromium (black, intensity multiplied by a factor of 4.7).

References.

S1. Velický, M.; Donnelly, G. E.; Hendren, W. R.; Mcfarland, S.; Scullion, D.; Debenedetti, W. J. I.; Correa, G. C.; Han, Y.; Wain, A. J.; Hines, M. A.; Muller, D. A.; Novoselov, K. S.; Abruña, H. D.; Bowman, R. M.; Santos, E. J. G.; Huang, F., Mechanism of Gold-Assisted Exfoliation of Centimeter-Sized Transition-Metal Dichalcogenide Monolayers. *ACS Nano* **2018,** *12*, 10463-10472.