



# Identification of individual and few layers of WS<sub>2</sub> using Raman Spectroscopy

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The Raman scattering of single- and few-layered WS<sub>2</sub> is studied as a function of the number of S-W-S layers and the excitation wavelength in the visible range (488, 514 and 647 nm). For the three excitation wavelengths used in this study, the frequency of the A<sub>1g</sub>(Γ) phonon mode monotonically decreases with the number of layers. For single-layer WS<sub>2</sub>, the 514.5 nm laser excitation generates a second-order Raman resonance involving the longitudinal acoustic mode (LA(M)). This resonance results from a coupling between the electronic band structure and lattice vibrations. First principle calculations were used to determine the electronic and phonon band structures of single-layer and bulk WS<sub>2</sub>. The reduced intensity of the 2LA mode was then computed, as a function of the laser wavelength, from the fourth-order Fermi golden rule. Our observations establish an unambiguous and nondestructive Raman fingerprint for identifying single- and few-layered WS<sub>2</sub> films.

Individual monolayers of transition metal dichalcogenides such as MoS<sub>2</sub> and WS<sub>2</sub> have recently caught the attention of the scientific community because these 2-dimensional semiconductors could have properties more attractive for specific applications than those of graphene<sup>1,2</sup> and boron nitride<sup>3,4</sup>. A single layer of MX<sub>2</sub> [M = (Mo or W) and X = (S, Se or Te)] typically contains one atomic layer of metal atoms with 6-fold in-plane coordination, hexagonally packed between two trigonal atomic layers of chalcogenide atoms. In single-layer form, the absence of interlayer coupling plus the lack of inversion symmetry (for supported films) leads to optical and electronic properties that differ markedly from those of the bulk<sup>5-9</sup>. For example, the electronic band structure transitions from indirect gap (in the bulk) to a direct gap in the monolayer<sup>7</sup>, and valley polarization (i.e. “valleytronics”) can be induced in monolayer MoS<sub>2</sub> by circularly polarized light<sup>10,11</sup>. While MoS<sub>2</sub> has received copious attention in the search for new properties and potential applications of 2D semiconductors<sup>8,9,12-19</sup>, little attention has been paid to monolayer and few-layer WS<sub>2</sub>. In this respect, we have recently demonstrated the synthesis of single-layer WS<sub>2</sub> triangular islands and observed intense room-temperature photoluminescence (PL) associated with specific edge terminations<sup>20</sup>. Although Raman spectroscopy has become a very powerful tool for studying graphene<sup>21-23</sup> and MoS<sub>2</sub><sup>13,17-19,24,25</sup>, the Raman scattering of single- and few-layered WS<sub>2</sub> still remains largely unexplored. Raman spectroscopy can not only be used to identify the number of layers<sup>13,21,22,25,26</sup>, but also probe subtle details in the electronic band structure and phonon dispersion through resonant Raman scattering<sup>21,27</sup>. Here we provide the first systematic study of the Raman response in monolayer and few-layer WS<sub>2</sub> as a function of the laser excitation wavelength. We report a novel resonant second-order Raman feature in single-layered WS<sub>2</sub> and discuss the general characteristics of the phonon modes that can provide a fingerprint for monolayer WS<sub>2</sub>.

## Results

As previously reported<sup>20</sup>, the synthesis of single- and few-layered WS<sub>2</sub> triangular 2D islands follows a two-step approach of thermal evaporation of tungsten trioxide (WO<sub>3</sub>) followed by sulfurization (see Methods section). The sample morphology, crystal structure and chemical composition were studied by means of scanning electron and transmission electron microscopy (SEM, TEM) (Figures 1a-c)<sup>20</sup>. Electron diffraction (inset in Figure 1b) reveals large single crystal domains with a high degree of crystallinity. Atomic force microscopy (AFM) was used to

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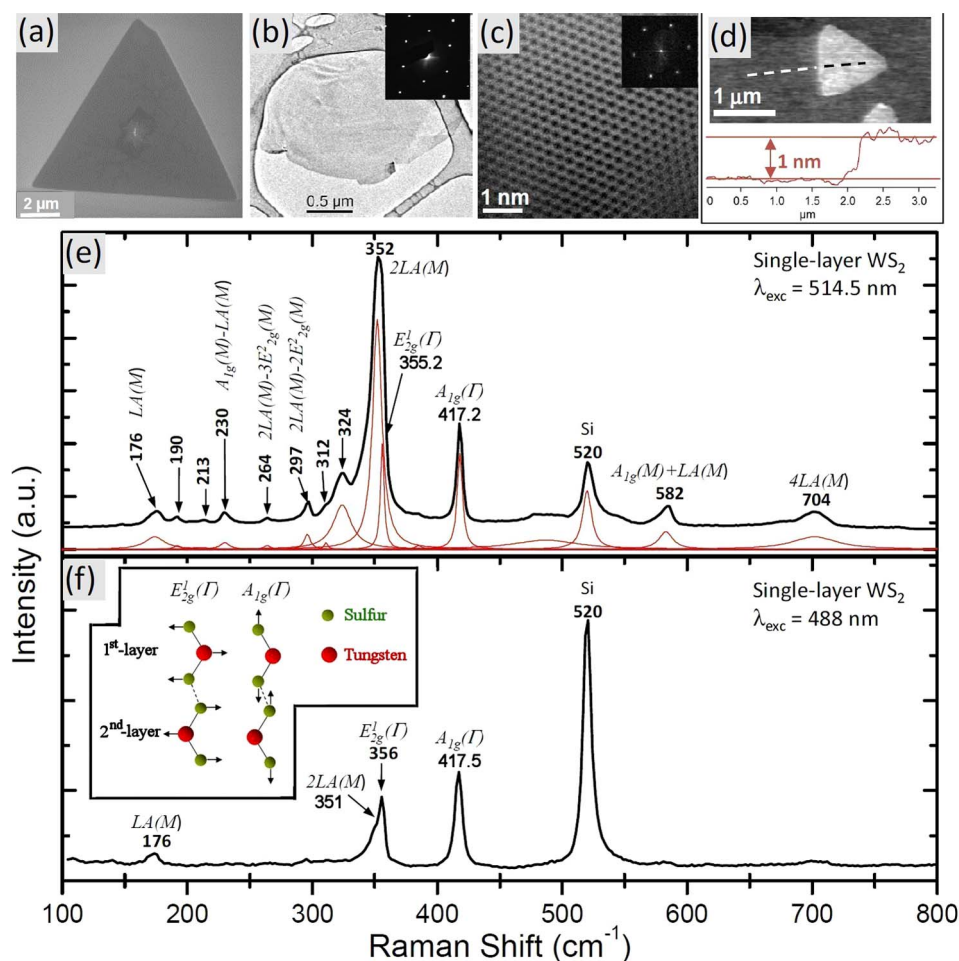
determine the number of layers within these WS<sub>2</sub> triangular islands (Figures 1d). We extract the thickness and wavelength-dependent behavior of the lattice vibrations in these 2D islands by correlating AFM images with Raman spectroscopy maps.

Raman spectra for bulk (i.e. multi-layered) WS<sub>2</sub> and MoS<sub>2</sub> have been previously studied. In a backscattering geometry, these spectra include first-order modes at the zone center ( $E_{2g}^1(\Gamma)$  and  $A_{1g}(\Gamma)$ ) plus a zone-edge mode – activated by disorder – which has been identified as the longitudinal acoustic mode at the M point, LA(M). The longitudinal acoustic phonons LA(M) are in-plane collective movements of the atoms in the lattice, similar to the sound waves. They are periodic compressions and expansions of the lattice that occur along the direction of propagation. The symbol (M) refers to the specific direction and magnitude of the momentum  $q$  of the phonon; in the phonon dispersion (frequency vs. momentum), they appear at the M-point of the Brillouin zone. Additional peaks correspond to multi-phonon combinations of these modes<sup>28–30</sup>. Previous reports on monolayer MoS<sub>2</sub> and chemically exfoliated WS<sub>2</sub><sup>14</sup> have focused exclusively on the first-order  $E_{2g}^1(\Gamma)$  and  $A_{1g}(\Gamma)$  optical modes. Resonant Raman scattering in single-layered dichalcogenides has not previously been observed.

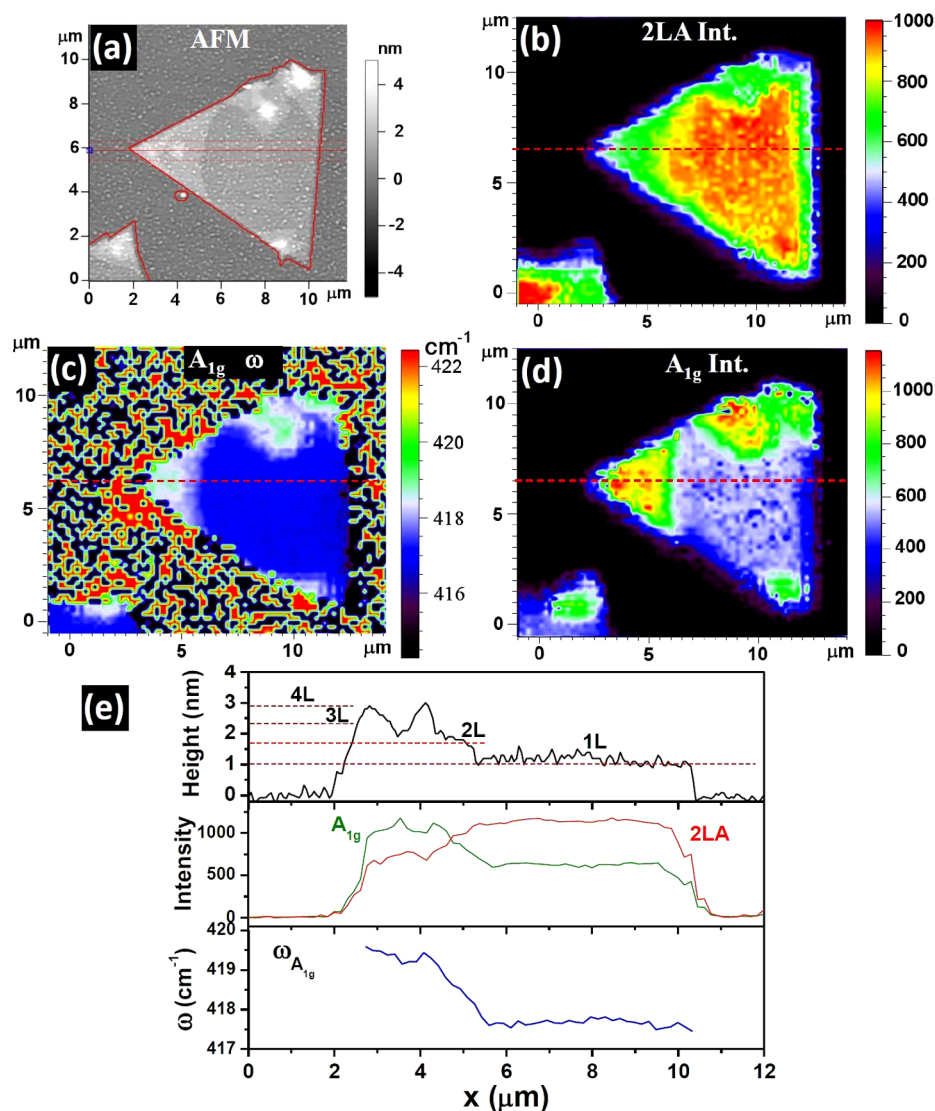
Figures 1e and f show typical Raman spectra of monolayer WS<sub>2</sub> regions using 514.5 nm and 488 nm excitation. For  $\lambda_{exc} = 488$  nm, the Raman spectrum is dominated by the first-order modes: LA(M)

at 176 cm<sup>-1</sup>,  $E_{2g}^1(\Gamma)$  at 356 cm<sup>-1</sup> and  $A_{1g}(\Gamma)$  at 418 cm<sup>-1</sup>. However, when monolayer WS<sub>2</sub> is excited at 514.5 nm, the Raman spectrum becomes very rich, revealing many second-order peaks that are stronger than those observed in the bulk material. Figures 1e and 1f give symmetry assignments for several peaks according to previous reports in bulk and fullerene-like WS<sub>2</sub> nanostructures. For  $\lambda_{exc} = 514$  nm, it is remarkable that the intensity of the strongest second-order Raman peak, the 2LA(M) mode at 352 cm<sup>-1</sup>, is approximately twice the intensity of the first-order  $A_{1g}(\Gamma)$ . Although the 2LA(M) mode overlaps with the first-order  $E_{2g}^1(\Gamma)$  mode at 356 cm<sup>-1</sup>, the multi-peak Lorentzian fitting shown in Figure 1e clearly separates their individual contributions.

The samples contain a large number of monolayer islands (1L), plus enough multilayer islands (see Figure 2a) to study the thickness dependence of the Raman response. The AFM height profile shown in Figure 2e confirms the presence of 1L, 2L, 3L and 4L regions within a single island. Raman mapping of this island at  $\lambda_{exc} = 514$  nm provides spatial maps of the 2LA(M) intensity and the  $A_{1g}(\Gamma)$  mode frequency and intensity, as shown in Figures 2b,c,d. The absolute intensity of the 2LA(M) mode increases with decreasing the number of layers, while the intensity of the  $A_{1g}(\Gamma)$  displays the opposite behavior. The softening of the  $A_{1g}(\Gamma)$  mode with decreasing number of layers (depicted in Figures 2c, e) presumably results from weaker interlayer contributions to the phonon restoring forces.



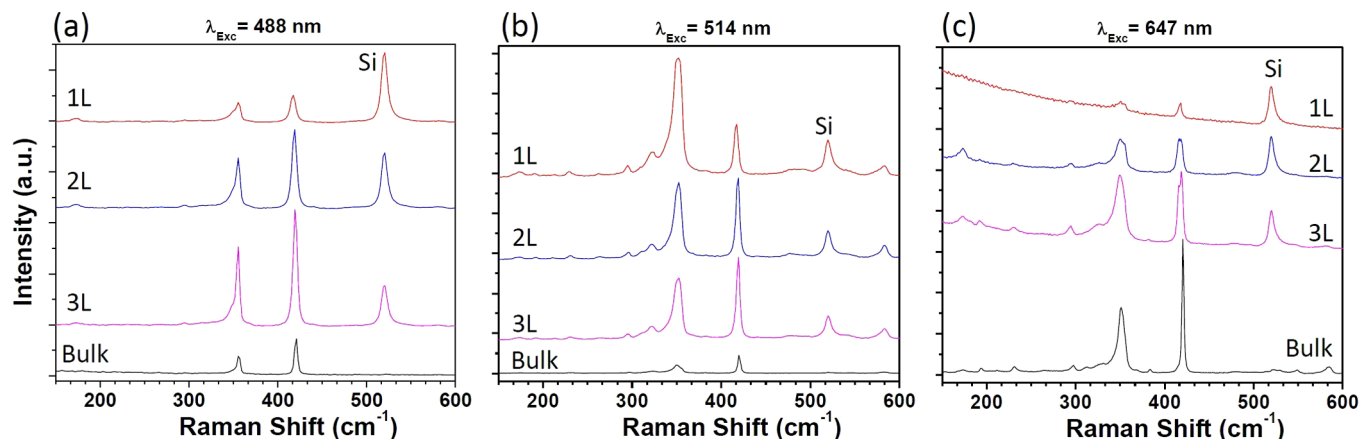
**Figure 1** | (a) SEM image of a monolayer WS<sub>2</sub> triangular island. (b) TEM image of a WS<sub>2</sub> island transferred to a lacey carbon grid with inset showing the electron diffraction pattern of the entire region. (c) High-resolution phase-contrast TEM image showing the hexagonal arrangement of the WS<sub>2</sub> structure with inset showing the Fourier transform of the micrograph. (d) AFM image of a WS<sub>2</sub> island and the corresponding height profile along the dashed line. (e) and (f) Room-temperature Raman spectra from a monolayer WS<sub>2</sub> region, using the 514.5 and 488 nm laser excitation, respectively, including Lorentzian peak fits for 514.5 nm data. The inset in (f) shows the atomic displacements for the in-plane phonon mode  $E_{2g}^1(\Gamma)$  and the out-of-plane phonon mode  $A_{1g}(\Gamma)$  for two adjacent layers, the dashed line represents the weak inter-layer van der Waals interaction.



**Figure 2** | (a) AFM image of a WS<sub>2</sub> triangular island, which varies from four to one layers thick. Also Raman mappings of the same WS<sub>2</sub> island (using 514.5 nm laser excitation): (b) intensity of the 2LA second-order mode, (c) frequency and (d) intensity of the A<sub>1g</sub> mode. (e) Line profiles along the red horizontal line in each image corresponding to height, 2LA intensity, A<sub>1g</sub> intensity and A<sub>1g</sub> peak position ( $\omega$ ). The Raman mappings as well as the intensity profiles refer to the maximum intensity of the peaks (not the integrated intensities).

Figure 3 summarizes the WS<sub>2</sub> Raman spectra as a function of island thickness and excitation wavelength. For  $\lambda_{\text{exc}} = 647$  nm, the absolute intensity of all Raman modes increases with the number of layers, which suggests that at this wavelength the Raman intensity is mainly affected by the scattering volume. A background related to the low-energy tail of the photoluminescence (which is centered around 630 nm<sup>20</sup>) appears for 3L and becomes more obvious in thinner samples. As reported in previous work<sup>20</sup>, room-temperature PL is associated with a transition from indirect-gap few-layer WS<sub>2</sub> to direct-gap monolayer WS<sub>2</sub>. Raman spectra taken with  $\lambda_{\text{exc}} = 488$  nm also showed an increase in the absolute intensity from 1L to 3L. However, the intensities for bulk are lower than for the 1L case. Such a behavior has been previously observed in graphene<sup>31</sup> and MoS<sub>2</sub><sup>13</sup> deposited on SiO<sub>2</sub>/Si substrates and is mainly attributed to optical interference in both the excitation laser and the Raman signal emitted by the sample. In contrast to these relatively familiar behaviors, the response at  $\lambda_{\text{exc}} = 514.5$  nm is a special case: the second-order Raman peaks, in particular the 2LA(M) mode, *increase* in intensity with decreasing number of layers and are largest in the monolayer.

We performed multi-peak Lorentzian fittings on each spectrum to obtain the thickness-dependent frequency of the main WS<sub>2</sub> Raman peaks (2LA(M), E<sub>2g</sub><sup>1</sup>( $\Gamma$ ) and A<sub>1g</sub>( $\Gamma$ )) for each wavelength, as shown in Figure 4a. The A<sub>1g</sub>( $\Gamma$ ) mode blueshifts when decreasing the number of WS<sub>2</sub> layers. This hardening of the A<sub>1g</sub> mode is consistent with the increasing restoring force caused by van der Waals interactions established among layers, and it is in agreement with previous results reported for MoS<sub>2</sub><sup>18</sup>. The E<sub>2g</sub><sup>1</sup>( $\Gamma$ ) and 2LA(M) phonon modes, however, exhibit very subtle blueshifts for a decreasing number of layers. It is worth noticing that in WS<sub>2</sub>, the close proximity of the 2LA(M) and E<sub>2g</sub><sup>1</sup>( $\Gamma$ ) increases the error in determining the frequency shift of both modes. The change in frequency is of the order of magnitude of the error bar, which is also affected by the fitting process, thus making more difficult to establish a clear frequency dependence with the number of layers. An anomalous behavior of the E<sub>2g</sub><sup>1</sup>( $\Gamma$ ) mode has been previously reported in few-layered MoS<sub>2</sub> films<sup>13,18,24</sup> and it might be caused by a stronger dielectric screening of the long-range Coulomb interactions between the effective charges in thicker samples<sup>25</sup>. A similar change in dielectric screening with the number of layers is expected for WS<sub>2</sub>.



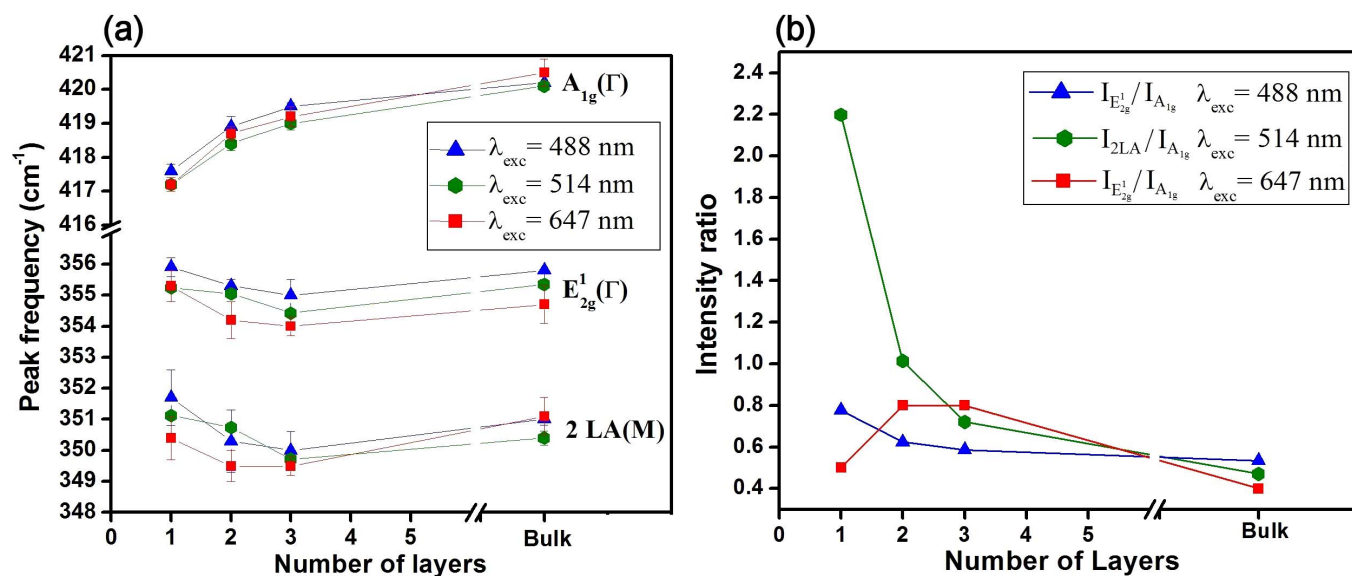
**Figure 3** | Raman spectra collected from regions with different WS<sub>2</sub> thicknesses (1L, 2L, 3L and bulk) using three different excitation wavelengths: (a) 488 nm, (b) 514.5 nm and (c) 647 nm. For each individual wavelength all the spectra, including that from the bulk, were acquired using the same experimental conditions of laser power and collection time.

We also studied the relative intensities of the strongest Raman peaks for each  $\lambda_{\text{exc}}$  as a function of the number of layers, as shown in Figure 4b. For  $\lambda_{\text{exc}} = 488$  nm and  $\lambda_{\text{exc}} = 647$  nm, the most intense features in the Raman spectrum correspond to the  $E_{2g}^1(\Gamma)$  and  $A_{1g}(\Gamma)$  modes and the intensity ratio  $I_{E_{2g}^1}/I_{A_{1g}}$  does not show major changes with the number of layers. The most interesting scenario again occurs for  $\lambda_{\text{exc}} = 514.5$  nm. In this case, the strongest Raman peaks are those associated with the  $2LA(M)$  and  $A_{1g}(\Gamma)$  phonon modes. The relative intensity  $I_{2LA}/I_{A_{1g}}$  increases dramatically for double- and single-layered films. We have repeated the experiment in different regions of the samples and also in WS<sub>2</sub> films suspended on a TEM grid; the ratio  $I_{2LA}/I_{A_{1g}}$  is always larger than 2 only in monolayer WS<sub>2</sub>. We attribute the intense  $2LA$  signal in monolayer WS<sub>2</sub> at  $\lambda_{\text{exc}} = 514.5$  nm to a double-resonant (DR) Raman process which is possible only in the specific electronic band structure of the monolayer, as described below.

Table 1 summarizes the frequency position for the main Raman modes as well as the intensity ratio for the most intense peaks, as a function of the number of layers and the excitation wavelength.

## Discussion

Figure 5 shows the phonon dispersion and electronic band structures for bulk and monolayer WS<sub>2</sub>, obtained using the density functional perturbation theory in the local density approximation. The experimental Raman peak at  $176$  cm<sup>-1</sup> falls in the range of the calculated zone-edge acoustic phonons. This mode has been identified with the longitudinal acoustic mode around the M point of the Brillouin zone<sup>28,30</sup>, although an alternative identification with the K point has been proposed by at least one group<sup>29</sup>. This finite-wavevector mode is presumably activated by disorder to become Raman active<sup>28</sup>. The precise doubling of frequency for the peak at  $352$  cm<sup>-1</sup> strongly suggests that such a peak is a second-order mode originating from the same phonon. The unique sensitivity of second-order resonant



**Figure 4** | Intensity ratios and peak frequencies of WS<sub>2</sub> Raman modes. (a) Frequencies of the  $A_{1g}(\Gamma)$ ,  $E_{2g}^1(\Gamma)$ , and  $2LA(M)$  Raman modes as a function of thickness (number of WS<sub>2</sub> monolayers) for the three excitation laser lines. Each point represents an average over ten different positions and the error bars correspond to the standard deviations (b) Thickness-dependent intensity ratios of  $I_{2LA}/I_{A_{1g}}$  (for  $\lambda_{\text{exc}} = 514.5$  nm) and  $I_{E_{2g}^1}/I_{A_{1g}}$  (for  $\lambda_{\text{exc}} = 488$  and  $647$  nm).



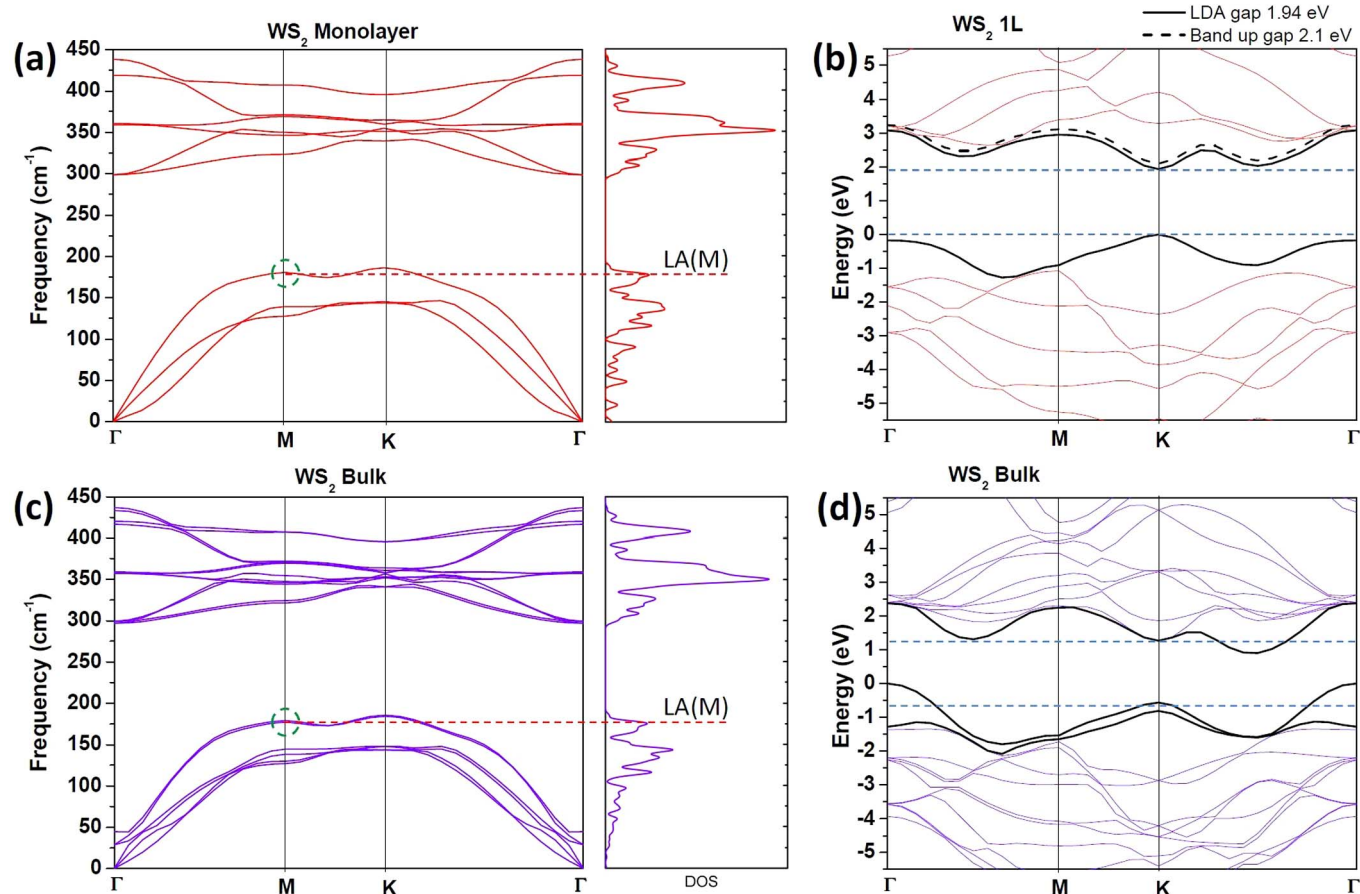
**Table 1** | Summary of the frequency position for the main Raman modes as well as the intensity ratio for the most intense peaks, as a function of the number of layers and the excitation wavelength

$\lambda_{\text{Exc}}$	Phonon modes	1-layer	2-layers	3-layers	Bulk
488 nm	$A_{1g}(\Gamma)$ ( $\text{cm}^{-1}$ )	417.5	418.9	419.5	420.2
	$E_{2g}^1(\Gamma)$ ( $\text{cm}^{-1}$ )	355.9	355.3	355	355.8
	$2LA(M)$ ( $\text{cm}^{-1}$ )	351.7	350.3	350	351
	$I_{E_{2g}^1}/I_{A_{1g}}$ (Intensity ratio)	0.78	0.62	0.59	0.53
514.5 nm	$A_{1g}(\Gamma)$ ( $\text{cm}^{-1}$ )	417.2	418.4	419	420.1
	$E_{2g}^1(\Gamma)$ ( $\text{cm}^{-1}$ )	355.2	355	354.4	355.3
	$2LA(M)$ ( $\text{cm}^{-1}$ )	351.1	350.7	349.7	350
	$I_{2LA}/I_{A_{1g}}$ (Intensity ratio)	2.2	1.01	0.72	0.47
647 nm	$A_{1g}(\Gamma)$ ( $\text{cm}^{-1}$ )	417.2	418.7	419.2	420.5
	$E_{2g}^1(\Gamma)$ ( $\text{cm}^{-1}$ )	355.3	354.2	354	354.7
	$2LA(M)$ ( $\text{cm}^{-1}$ )	350.4	349.5	349.5	351.1
	$I_{E_{2g}^1}/I_{A_{1g}}$ (Intensity ratio)	0.5	0.8	0.8	0.4

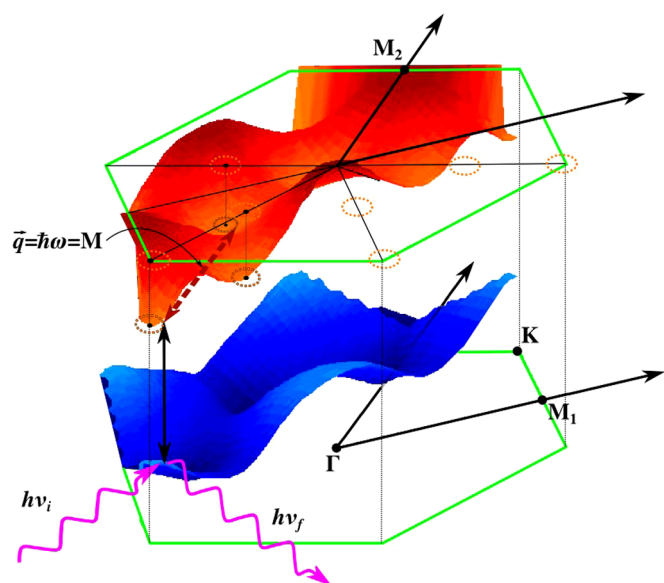
Raman processes to precise phonon wavevectors enables us to unambiguously identify the second-order  $352 \text{ cm}^{-1}$  peak (and by extension, the first-order  $176 \text{ cm}^{-1}$  peak) with the M-point LA phonon, as described below.

The double resonant Raman process involves two phonons with equal and opposite momentum and an intermediate excited electronic state that resonates with the electronic band structure (in

addition to the resonance for the initial optical transition, hence the term double resonance). For a second-order Raman process to satisfy the requirements for double resonance, the optical excitation energy must match a vertical electronic transition (vertical black arrows in Figure 6) and the conduction band must contain quasi-isoenergetic electronic states (dashed red arrows in Figure 6) at a momentum difference corresponding to the phonon momentum  $\pm q$



**Figure 5** | Phonon dispersion plus density of states [left]; and electronic band structures [right] for  $\text{WS}_2$  monolayer [top] and bulk [bottom], respectively. The electronic band structure in (b) was calculated by LDA with 1.94 eV band gap; the dashed line corresponds to the bottom of the conduction band with a rigid shift to match the experimental 2.1 eV band gap. Although the phonon dispersions for monolayer and bulk are very similar, their band structures are clearly different. While the direct gap at the K point remains almost the same; the electronic bands between  $\Gamma$ -M and  $\Gamma$ -K undergo major changes associated with the indirect-to-direct bandgap transition from bulk to monolayer. The horizontal dashed lines in (b) and (d) are guides for the eye to visualize better these differences.

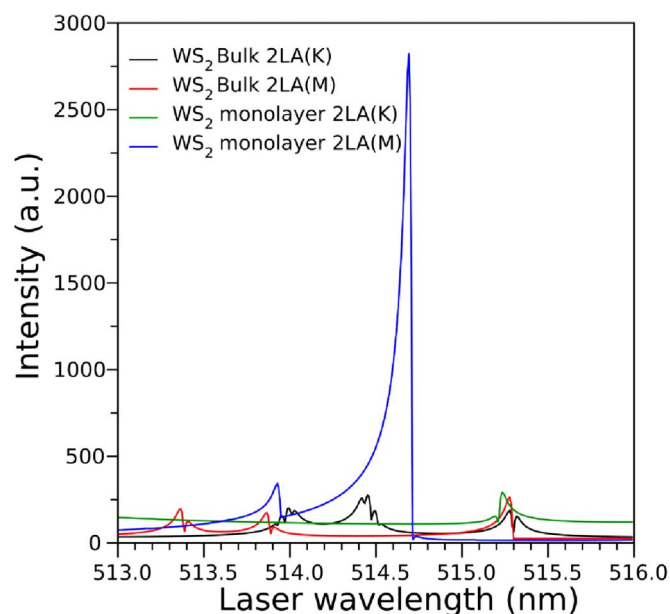


**Figure 6** | Schematic of the double-resonant Raman process that generates the 2LA(M) experimental peak. Calculated data from the valence (blue) and conduction (red) bands are used for the visualization. An incident photon with energy  $h\nu_i$  produces a vertical electronic transition (black vertical arrow) from valence to conduction band. The electron in the conduction band then experiences two electron-phonon scattering events, the first scattering event involving a phonon with momentum  $+q$  and the second involving a phonon with momentum  $-q$  (red dashed double arrow). Finally another vertical transition from conduction to valence band emits a Raman-shifted photon with energy  $h\nu_f$ .

(or similarly for the valence band in the case of phonon-hole scattering). The momentum dependences of the electronic structure and phonon dispersion must combine to produce sharp peaks in momentum space for the double resonant process, in order to produce a sharp Raman feature.

Since the most important structure in the double-resonant process typically arises from the complex interplay of electron and phonon dispersion relations, the essential features of double-resonant Raman processes can be captured in a ‘reduced’ calculation under a simplifying assumption of constant scattering matrix elements for the component scattering events. Thus the *ab initio* electronic and phonon band structures can be used to compute the reduced intensity of the 2LA mode from the fourth-order Fermi golden rule – for details, see the Methods section. The numerical results corresponding to this model are summarized in Figure 7, where the reduced intensity of the 2LA double resonant mode at different  $q$ -points is plotted as a function of the laser wavelength. The reduced intensities for the bulk and the monolayer were investigated in the vicinity of the three laser excitations: 488, 514.5 and 647 nm. At 488 and 647 nm the Raman intensity of the bulk is always greater than the monolayer (not shown). However, the monolayer exhibits a pronounced resonant peak close to 514.7 nm. Furthermore, by restricting the phonon wavevectors allowed in the calculation, it is possible to clearly identify the reciprocal space location of the dominant phonon contributions to the double resonance. In particular, Figure 7 compares the contributions from phonons in the vicinity of K and M; the dominance of the M-point contribution is obvious, which justifies the identification of this process with 2LA(M).

In the bulk system, changes in the electronic structure drive the system out of resonance for both electron-phonon and hole-phonon mediated processes. In Figure 5(b) and 5(d) we can see that the direct gap at the K point remains almost the same; however, the electronic bands between  $\Gamma$ -M and  $\Gamma$ -K undergo major changes originating



**Figure 7** | Reduced Raman intensity of the 2LA Raman line at the vicinity of K and M as a function of laser energy using a double-resonant model for both bulk and monolayer  $WS_2$ . Although the reduced intensities were also investigated around 488 and 647 nm (not shown), the monolayer system shows a resonant peak only for the vicinity of 514.7 nm.

from the indirect-to-direct bandgap transition when the system transitions from bulk to monolayer. This tendency persists after a small rigid shift of the conduction band has been applied to correct the well-known DFT underestimation of the band gap and match the experimental gap of 2.1 eV<sup>32</sup>, which is similar to the GW-corrected direct gap of 2.1 eV<sup>33</sup>.

In summary, we have systematically studied the thickness- and wavelength-dependent Raman behavior for newly synthesized single- and few-layered two-dimensional  $WS_2$  crystals. Our results reveal that the  $A_{1g}(\Gamma)$  mode softens while the 2LA(M) and  $E'_{2g}(\Gamma)$  modes present a very subtle hardening with decreasing number of  $WS_2$  layers. The analysis presented here unambiguously confirms that the 176  $cm^{-1}$  feature arises from an M-point phonon. In addition, a striking increase in the intensity of the 2LA(M) mode occurs with 514 nm laser excitation. This behavior can be explained in terms of a double resonance process which is active only in the monolayer. Both frequency shifts and changes in relative intensity can provide an unambiguous, nondestructive identification of monolayer  $WS_2$ . The more singular dispersion relations of electrons and phonons in two dimensions (as compared to three) facilitate the generation of sharp Raman features via a complex double-resonant process. This mechanism may be more broadly applicable in characterizing the structural, electronic and vibrational properties of other layered systems.

## Methods

**Synthesis.**  $WO_3$  thin films (5–20 Å) were thermally deposited on  $SiO_2/Si$  substrates in high vacuum ( $10^{-5}$ – $10^{-6}$  Torr). Subsequently, the films were transferred into a quartz tube reactor. During the sulfurization of the  $WO_3$  films, samples were kept at 800 °C for 30 min under an Argon flow and S vapors were generated from S powders placed up-stream in a lower temperature region ( $\sim 250$  °C) which was independently controlled.

For the TEM observations, we transferred as-grown  $WS_2$  islands onto gold Quantifoil® TEM grids (from SPI), which contain a polymer thin film with 2  $\mu m$  periodic holes. The  $WS_2$  islands were released from the original  $Si/SiO_2$  wafer by two methods, both of which involved etching in 15 M KOH. The first approach<sup>34</sup> spin-coats the wafer with a PMMA solution (495k) at 3000 RPM for 30 seconds. The polymer was then allowed to cure overnight at room temperature. The edge of the wafer was marked with a sharp blade to expose the  $Si/SiO_2$  surface and the wafer was subsequently immersed in 15 M KOH. The PMMA/ $WS_2$  film was released by the



effect of the caustic solution and could be fished out with the TEM grid. The TEM grid was then placed on absorbent paper and thoroughly washed with deionized water. Finally, the PMMA was dissolved with acetone droplets. In an alternative PMMA-free approach<sup>35</sup>, the TEM grid was placed on the Si/SiO<sub>2</sub> wafer containing the WS<sub>2</sub> islands. One drop of IPA was allowed to dry on the TEM grid and after 10 minutes the wafer was immersed in 15 M KOH. The grid was released and placed on absorbent paper and washed thoroughly with deionized water.

**Characterization.** WS<sub>2</sub> films were characterized by Raman and PL spectroscopies performed in a Renishaw in Via confocal microscope-based Raman spectrometer with a spectral resolution better than 1 cm<sup>-1</sup>. We used 488, 514.5 and 647 nm laser excitations, keeping the laser power under 0.2 mW at all times. The 520 cm<sup>-1</sup> phonon mode from the silicon substrate was used for calibration. The Raman spectra for the bulk were collected from WS<sub>2</sub> powder, 99% (Sigma-Aldrich). High-resolution transmission electron microscopy was carried out in a JEOL 2010F equipped with an energy dispersive X-ray (EDX) spectrometer, with an accelerating voltage of 200 kV, field-emission source, ultra-high resolution pole piece (Cs = 0.5 mm), and a 1.9 Å Scherzer limit. SEM observations were performed in a FEI XL30 SEM at 6 kV and an LEO 1530 FESEM operated at 1 kV. Non-contact atomic force microscopy was performed in a MFP-3D-SA from Asylum Research.

**Theoretical modeling.** Electronic structure calculations are carried out using density functional theory in the local density approximation, with the Ceperley and Adler exchange correlation functional parametrized by Perdew and Zunger, as implemented in the plane-wave code CASTEP<sup>36</sup> within Materials Studio 5.5 (software by Accelrys at accelrys.com). The structures are geometrically optimized until the energy difference reached  $5 \times 10^{-6}$  eV/atom with a maximum force of 0.01 eV/Å. The plane wave cutoff energy was 720 eV with a norm-conserving pseudopotential on a grid of  $9 \times 9 \times 2$  k-points and a FFT grid of  $30 \times 30 \times 108$  for the WS<sub>2</sub> crystal and  $30 \times 30 \times 180$  for the WS<sub>2</sub> isolated layer; (the WS<sub>2</sub> layer has a larger cell in the c direction). The phonon density of states and dispersion curves were calculated with the above parameters using density functional perturbation theory as implemented in CASTEP, using a linear response methodology that works well for insulators<sup>37</sup>.

The optimized unit cell lattice parameters for the WS<sub>2</sub> crystal are  $a = b = 3.147 \text{ \AA}$  and  $c = 12.167 \text{ \AA}$ , while the experimental values reported are:  $a = b = 3.153 \text{ \AA}$  and  $c = 12.323 \text{ \AA}$ .<sup>38</sup> For the WS<sub>2</sub> monolayer, the calculated  $a$  and  $b$  parameters ( $a = b = 3.146 \text{ \AA}$ ) are almost the same as those for the bulk crystal. The distance between the layers is set to 20 Å to eliminate interlayer interaction.

The double resonant Raman reduced intensities of the 2LA mode were modeled using the Fermi golden rule generalized to fourth order<sup>37</sup>. Electron-two-phonon-electron, electron-two-phonon-hole, and hole-two-phonon-hole processes were considered. The scattering matrix elements were held constant, so that, one summand of  $I^{PP}$  of the electron-electron two-phonon process is expressed as:

$$\frac{1}{N_k N_q N_c N_v N_\mu} \sum_{k,q,c,v,\mu} \frac{1}{(\epsilon_L - \epsilon_k^c + \epsilon_k^v - \hbar\omega_{-q}^v - \hbar\omega_q^c - i\frac{\gamma}{2}) (\epsilon_L - \epsilon_{k+q}^c + \epsilon_k^v - \hbar\omega_{-q}^v - i\frac{\gamma}{2}) (\epsilon_L - \epsilon_k^c + \epsilon_k^v - i\frac{\gamma}{2})}$$

The sum is over k-points  $k$ , q-points  $q$ , valence bands  $v$ , conduction bands  $c$  and phonon branches  $\nu$  and  $\mu$ . For the bulk WS<sub>2</sub> structure, 234 k-points were used to sample the Brillouin zone, the three highest valence bands, the three lowest conduction bands, and two phonon branches over 24 q-points. For monolayer WS<sub>2</sub>, 234 k-points were also used to sample the Brillouin zone, the two highest valence bands, the two lowest conduction bands, and one phonon branch over 12 q-points. The reduced intensity is computed as the sum over all possible processes using the density functional theory band structure after a small rigid shift was applied to the conduction bands to account for the well-known underestimation of the calculated band gap within DFT. Only the electron-two-phonon-electron processes are found to contribute significantly to the difference in intensity between the monolayer and the bulk.

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### Author contributions

M.T., H.T. and H.R.G. designed the experiments. The synthesis of the samples was carried out by N.P.L., H.R.G. and A.L.E. The Raman spectra were acquired by A.B. and H.R.G. Theoretical calculations were performed by H.T., F.L.U., A.R.B.M., J.-C.C., V.C. and C.-I.C.

AFM characterization was performed by B.W. and H.R.G. TEM sample preparation was carried out by A.L.E. and H.R.G. TEM observations were carried out by H.R.G. SEM characterization was carried out by A.L.E. and N.P.L. All the authors contributed to the manuscript preparation and discussion of results.

### Additional information

**Competing financial interests:** The authors declare no competing financial interests.

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