

Dielectric nano-antennas for strain engineering in atomically thin two-dimensional semiconductors

Luca Sortino,^{*,†} Matthew Brooks,[‡] Panaiot G. Zotev,[†] Armando Genco,[†] Javier Cambiasso,[¶] Sandro Mignuzzi,[¶] Stefan A. Maier,^{¶,§} Guido Burkard,[‡] Riccardo Sapienza,[¶] and Alexander I. Tartakovskii^{*,†}

[†]*Department of Physics and Astronomy, University of Sheffield, Sheffield, S3 7RH*

[‡]*Department of Physics, University of Konstanz, D-78464 Konstanz, Germany*

[¶]*The Blackett Laboratory, Department of Physics, Imperial College London, London, SW7 2BW*

[§]*Chair in Hybrid Nanosystems, Nanoinstitut München, Faculty of Physics, Ludwig-Maximilians-Universität München, 80539 München, Germany*

E-mail: l.sortino@sheffield.ac.uk; a.tartakovskii@sheffield.ac.uk

Abstract

Atomically thin two-dimensional semiconducting transition metal dichalcogenides (TMDs) can withstand large levels of strain before their irreversible damage occurs. This unique property offers a promising route for control of the optical and electronic properties of TMDs, for instance by depositing them on nano-structured surfaces, where position-dependent strain can be produced on the nano-scale. Here, we demonstrate strain-induced modifications of the optical properties of mono- and bilayer TMD WSe₂ placed on photonic nano-antennas made from gallium phosphide (GaP). Photoluminescence (PL) from the strained areas of the TMD layer is enhanced owing to the efficient coupling with the confined optical mode of the nano-antenna. Thus, by following the shift of the PL peak, we deduce the changes in the strain in WSe₂ deposited on the nano-antennas of different radii. In agreement with the presented theory, strain up to $\approx 1.4\%$ is observed for WSe₂ monolayers. We also estimate that $> 3\%$ strain is achieved in bilayers, accompanied with the emergence of a direct bandgap in this normally indirect-bandgap semiconductor. At cryogenic temperatures, we find evidence of the exciton confinement in the most strained nano-scale parts of the WSe₂ layers, as also predicted by our theoretical model. Our results, of direct relevance for both dielectric and plasmonic nano-antennas, show that strain in atomically thin semiconductors can be used as an additional parameter for engineering light-matter interaction in nano-photonic devices.

Keywords

transition metal dichalcogenides, dielectric nanoantennas, exciton, strain engineering, photoluminescence

Control over lattice distortions in semiconductors, or strain-engineering, offers valuable tools for tailoring their electronic and optical properties. The exceptional flexibility of atomically thin two-dimensional (2D) crystals¹ has opened the way to employ mechanical deformation for engineering their physical properties,²⁻⁷ and has made them promising for applications in flexible electronics.^{8,9} Among 2D semiconductors, the family of transition metal dichalcogenides¹⁰ has shown attractive properties including an indirect-to-direct bandgap transition in monolayers,^{11,12} tightly bound excitons¹³ and coupling between the spin and valley degrees of freedom.¹⁴ Single layers of TMDs, only three atoms thick, have been observed to withstand large strain levels ($>10\%$)¹⁵ before fracture, offering a unique possibility to engineer their electronic band structure using strain.¹⁶⁻²⁰ This approach has been successfully applied for modifying their optical properties,²¹⁻²⁶ tuning carrier mobilities²⁷ and controlling the charge transport.^{28,29} Furthermore, spatial variation of the strain in TMD layers, occurring due to imperfections of fabrication methods or introduced intentionally, translates into a position dependent bandgap.^{30,31} This was shown to result in periodically modulated optical properties in monolayer MoS₂ placed on pre-patterned substrates,³² as well as to give rise to funnelling of excitons into the areas with a larger tensile strain,^{33,34} where the lowest exciton energy is achieved. Finally, in mono- and bi-layer WSe₂ and WS₂ placed on silica or polymer nano-pillars, single photon emitting defects were readily observed, whose origin was thus linked with the strain induced in the few-layer semiconductor.^{35,36}

While initial demonstrations of strained 2D semiconductors in electronic devices have been reported,^{27,37} the use of strain to control the optical properties of TMDs in nano-photonic systems has been largely unexplored.³⁸ One of the approaches to engineer light-matter interaction relies on the use of nano-antennas,³⁹⁻⁴¹ which can confine light in volumes below the diffraction limit.⁴² The strong confinement of the electric field at the hot-spots of the nano-antenna, enhances the light-matter interaction for the emitters positioned within the volume of its optical mode.⁴³⁻⁴⁵ While these phenomena have been extensively studied for surface plasmons in metals,^{46,47} recently high-refractive-index dielectric nano-photonic

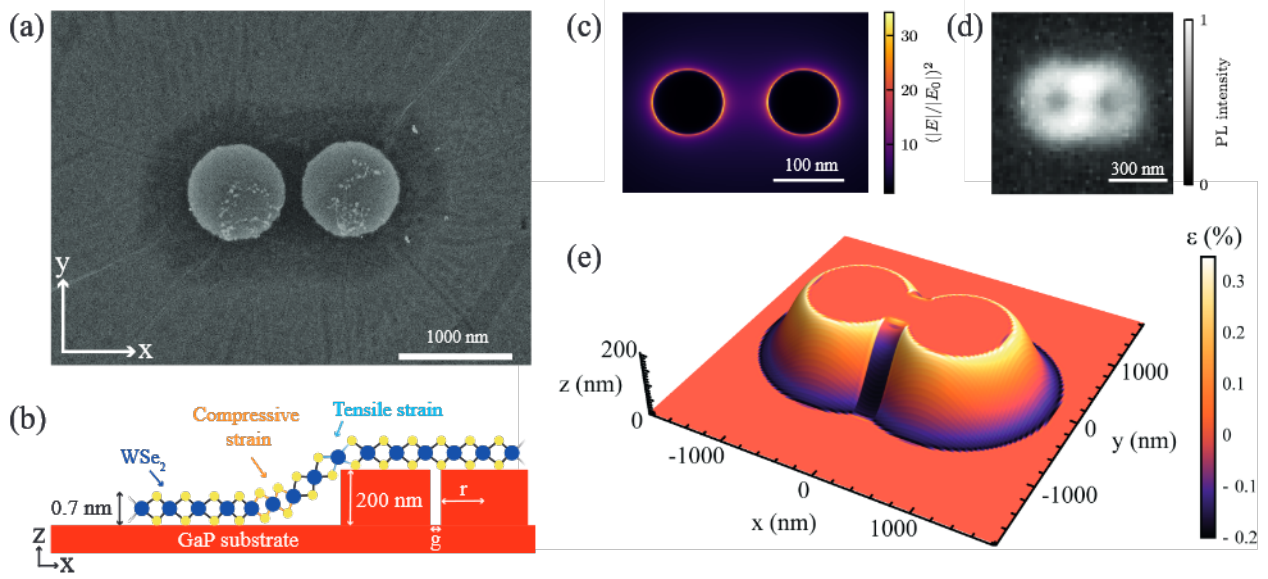


Figure 1: (a) Scanning electron microscope image of a GaP dimer nano-antenna (top view) with a radius $r=400$ nm, covered with 2L-WSe₂. Scale bar: 1 μ m. The darker area around the nano-pillars is the suspended 2D layer stretching from the substrate up to the top surface of the nano-antenna. (b) Schematic of a GaP dimer nano-antenna shown in red with a monolayer of WSe₂ transferred on its top. The areas of high compressive and tensile strain are labelled. (c) The ratio of the intensities of the scattered and incident electro-magnetic waves shown as the ratio of the corresponding electric fields $(|E|/|E_0|)^2$ for a GaP dimer nano-antenna with $r=50$ nm under 685 nm unpolarized excitation. The presented field distribution is calculated at the top of the dimer ($z=200$ nm) with a finite-difference time-domain software (Lumerical Inc.). Scale bar: 100 nm. (d) Photoluminescence image of a GaP nano-antenna ($r=300$ nm) covered with monolayer WSe₂. The brightest PL is observed where the tensile strain and near-field enhancement are co-located and maximized. Scale bar: 600 nm. (e) Calculated strain ε for a monolayer WSe₂ placed on top of a dimer nano-antenna with $r=500$ nm. The middle of the gap corresponds to $x=0$ and $y=0$.

structures⁴⁸ have rapidly gained attention as they offer low losses^{49,50} and both electric and magnetic Mie-type optical resonances.⁵¹ Recent reports of dielectric nano-antennas interfaced with 2D TMDs showed modified PL directionality in monolayer MoS₂ coupled to silicon nano-rods,⁵² as well as strong PL and Raman signal enhancement for WSe₂ placed on top of GaP dimer nano-pillars.⁴³ In this work, we investigate the role of strain in the latter case of the dimer structures. Compared with a more trivial case of single pillars, which can also be used to provide local strain,^{35,36} the dimer nano-pillars provide stronger light-matter interaction with more interesting photonic properties,⁴³ thus motivating our study.

Contrary to previous approaches employing bending apparatuses,²¹ piezoelectric substrates⁵³ or relying on the difference of the thermal expansion coefficients,^{54,55} here we demonstrate that dimer nano-antennas can be used to strain a 2D semiconducting layer, while at the same time the PL from the strained material is enhanced via the coupling with the optical mode of the nano-antenna.⁴³ We study both experimentally and theoretically monolayers (1L) and bilayers (2L) of TMD WSe₂ transferred on closely spaced (<100 nm) pairs of nano-pillars, referred to as dimers^{43,56} below (see Figs.1a-d). The co-location between WSe₂ tensile deformation and the maximum of the near-field enhancement of the antenna at the edges of the top surface of the pillars (Fig.1b-e), allows clear observation of the strain-induced band structure modifications in PL. We demonstrate a dependence of the amount of strain induced in the TMD layer by nano-antennas of different radii. With this approach we observe the tuning of the intralayer exciton in monolayer WSe₂ exceeding 50 meV, corresponding to the uniaxial tensile strain up to $\approx 1.4\%$.⁵⁷ These findings are supported by our model based on the continuum-mechanical plate theory approach,^{58,59} which we use to calculate the strain distribution in 1L and 2L-WSe₂ placed on the nano-antennas. Using this theory we predict higher strain in the bilayers than in monolayers placed on the nano-antennas of the same radius. Tensile strain $> 3\%$ is calculated for 2L-WSe₂ placed on the nano-antenna with $r = 50$ nm, for which we experimentally observe abrupt changes in the PL spectrum consistent with the transition to the direct bandgap. From the calculated topography model, we deduce the position-dependent band structure induced in the WSe₂ and predict occurrence of strain-induced potential wells at the nano-pillar edges, which can trap the excitons. This behaviour is confirmed in the cryogenic PL measurements of 2L-WSe₂, which exhibits localization of the excitonic PL, consistent with the predicted potential shape. Further to demonstrating tuning of strain in TMDs using all-dielectric nano-antennas of various dimensions, our findings have direct relevance to TMDs coupled to plasmonic structures, where similarly both the strain and the enhanced optical fields may be co-located.^{60,61}

Results

Strained WSe₂ coupled with GaP nano-antennas Fig.1a shows an electron microscopy image of the top view of a GaP dimer nano-antenna with an atomically thin WSe₂ bilayer deposited on top. Owing to its elasticity, the thin semiconductor crystal stretches from the substrate up to the topmost edge of the nano-antenna, without compromising its integrity. Fig.1b shows a schematic diagram of a WSe₂ monolayer (0.7 nm thick) transferred on top of a GaP dimer nano-antenna. We use nano-antennas with a height of 200 nm, a radius varying from 50 to 500 nm and a gap from 50-100 nm. Due to the height mismatch between the substrate and the top surface of the antenna, the WSe₂ layer experiences a local compressive or tensile deformation, as shown in Fig.1b,e. The optical response of a dimer nano-antenna exhibits spectrally broad resonances^{43,56} (see calculated spectra in Supplementary Note I). Fig.1c shows the spatial intensity distribution of the scattered light of a nano-antenna illuminated with a planar wave at the top surface of a GaP dimer nano-antenna under unpolarized excitation. We present this scattered intensity as $(|E|/|E_0|)^2$, where E is the electric field in the scattered wave, and E_0 is the electric field of the plane wave illuminating the structure. Maxima of the field intensity are located at the edges of each nano-pillar and inside the gap region between them. The transferred 2D semiconductor layer stretches over the nano-structure, fully overlapping with the confined optical modes.⁴³ An optical microscope image of 1L-WSe₂ PL emission on top of a single GaP dimer nano-antenna, with $r = 300$ nm and $g = 65$ nm, is shown in Fig.1d (see Methods and Ref.⁶² for more details). In this image it is possible to resolve the spatial distribution of the PL signal which closely resembles that of the enhanced field in Fig.1c.

We describe the nano-scale distortions in the 2D layer with an approach based on the continuum-mechanical plate theory⁵⁸ by modelling the pressure experienced by the stretched semiconductor in the out-of-plane direction (see Supplementary Note II for the full description of the model). From the analytically calculated function for a single pillar, we interpolate to the low-symmetry dimer structure and calculate the spatial distribution of strain intro-

duced in the stretched semiconductor crystal. The resulting strain topography for a 1L-WSe₂ placed on top of a dimer nano-antenna is shown in Fig.1e. The tensile strain reaches its maximum at the topmost edge of each nano-pillar, at a height $z = 200$ nm, co-located with the largest near-field enhancement produced by the underlying nano-antenna. The regions of compressive strain are located where the 2D layer touches the substrate, at $z \approx 0$, and inside the gap region between the pillars.

In what follows, we show that the co-location of the maximum of the confined optical mode and that of the tensile deformation in the 2D layer, allows us to directly probe the strain-induced band structure renormalization by monitoring the enhanced excitonic room temperature PL emission for both 1L and 2L-WSe₂. At cryogenic temperature, we show the exciton PL localization in 2L-WSe₂ in the regions of the largest tensile strain where the reduction of the exciton energy is the strongest, as predicted by our theoretical model.

Strain tuning in 1L-WSe₂ coupled to GaP nano-antennas We studied the emission from the same nano-antenna shown in Fig.1 in a micro-PL setup at room temperature using PL mapping with a micron resolution (see Methods), as shown in Fig.2a. The sample is excited at $\lambda_{exc} = 685$ nm, below the absorption edge of GaP, and thus this light is only absorbed by the WSe₂ layer. As expected, a large enhancement in the overall WSe₂ PL intensity is correlated with the location of the nano-antenna. Note, that in contrast to Fig.1d, here the resolution is limited by the excitation spot size ($r \approx 1$ μ m). As shown in Fig.2b, we extract the peak maxima from the PL map in Fig.2a and observe a prominent red-shift of the intralayer exciton (also referred to as 'A exciton') peak on the nano-antenna. This effect is expected from the reduction of the WSe₂ bandgap under tensile strain. As schematically shown in Fig.2c, the direct optical transition in 1L-WSe₂ is located at the K(K') point of the Brillouin zone.^{11,12} Under the increasing tensile strain, the bandgap is expected to reduce^{24,25} mainly due to the lowering of the conduction band minimum, as a consequence of the change in the electronic orbital overlap following the changes in the atomic bond lengths and angles.^{17,18,20} Strain induced by underlying nano-structures

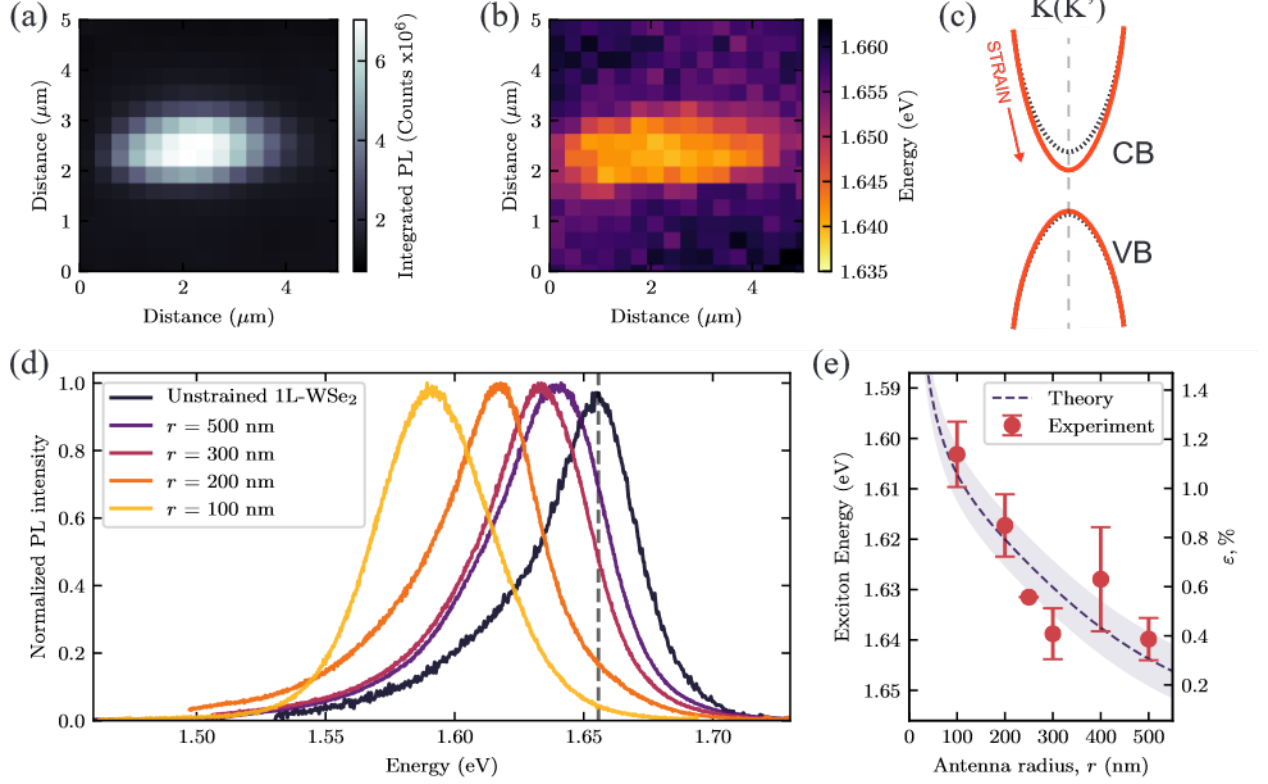


Figure 2: (a) PL intensity map for 1L-WSe₂ placed on a GaP nano-antenna with $r = 300$ nm measured using a micro-PL set-up. (b) The same map as in (a), but showing the exciton peak energy distribution. (c) Schematics showing how the band-structure around the K valley in 1L-WSe₂ is modified under tensile strain (red). The band-structure for the unstrained 1L-WSe₂ is shown in black. (d) Normalized PL spectra for 1L-WSe₂ placed on top of nano-antennas with different radii r . The red-shift observed for decreasing r corresponds to increasing strain in WSe₂. (e) Red circles show the average PL peak positions for 1L-WSe₂ placed on nano-antennas with different radius and corresponding uniaxial strain deduced using the experimental gauge factor from Ref.⁵⁷ The error bars represent the standard deviation between different dimers of the same radius. The dashed line shows the strain values calculated using our theoretical model. The shaded region corresponds to a value of $\pm 0.1\%$ of strain around the theoretical curve, equal to the average standard deviation found in experiments.

has previously been measured using Raman enhancement in graphene on plasmonic nano-antennas.^{63,64} As we show in Supplementary Note III, we collected the Raman scattering signal from the strained 1L-WSe₂ and observe a shift of the Raman peak, as expected for tensile strain.⁶⁵

From our theoretical description we have derived a dependence of the tensile strain max-

imum, located at the nano-pillar edges, on the nano-antenna size (see Supplementary Note II). We found that by reducing the nano-pillar radius an increased strain is introduced in the 2D layer. We confirm this trend experimentally in Fig.2d which shows the normalized 1L-WSe₂ PL spectra for the TMD coupled to nano-antennas of different radii (see also Supplementary Note IV for raw PL spectra and more PL characterization data). For comparison we also show the PL spectrum for WSe₂ on a planar GaP substrate, where the intralayer exciton peak is marked by a dashed line. When the nano-pillar radius is reduced, the larger red-shift in the exciton PL peak confirms that the semiconducting layer is experiencing an increased strain, as predicted by our model.

By using the previously experimentally observed gauge value for the WSe₂ intralayer A exciton red-shift as a function of strain of -49 ± 2 meV/%,⁵⁷ we extract the uniaxial tensile strain magnitude for WSe₂ placed on the nano-antennas with different radii. As shown in Fig.2e, we find tensile strain values up to $\approx 1.4\%$ as the nano-antenna radius is reduced, comparable to the estimate from our theoretical model shown with the dashed line. There is a variation in the peak position measured on different pillars. This effect can be attributed to the non-uniform coverage of the antenna surface by the monolayer and from the local disorder introduced in the WSe₂ layer for instance from wrinkles, contamination etc. Further variation may occur due to imperfections in fabrication of the nano-antennas. These effects are also responsible for additional broadening of the PL linewidth, which is otherwise expected to reduce in WSe₂ monolayers under uniform strain.⁵⁷

Direct bandgap transition in 2L-WSe₂ As schematically shown in Fig.3a, using the band-structure picture without excitonic effects, contrary to the monolayer case, a WSe₂ bilayer is an indirect bandgap semiconductor. It exhibits two main recombination pathways at room temperature, a momentum direct (higher energy) and indirect (lower energy) transition, respectively involving the K and Q points of the conduction band.¹⁶ For unstrained 2L-WSe₂ (black dashed line) the lowest energy transition is the phonon-assisted recombination between the conduction band minimum at the Q point and the valence band maximum

at the K point. Under tensile strain (coloured lines in Fig.3a), similar to the monolayer case, the conduction band minimum at the K point exhibits a reduction in energy, leading to a transition from the indirect to direct bandgap in highly strained 2L-WSe₂.^{65,66} In previous reports, there were contrasting interpretations for the dependence of the Q valley energy on strain.^{65,66} In Fig.3a we use the interpretation from Ref.,⁶⁶ thus assuming that the Q valley energy would reduce under the tensile strain. However, the tuning of the Q valley is found to be negligible in the range of strain investigated in our samples (see more detailed PL spectra analysis in Supplementary Note V). The bandgap behaviour is thus determined by the stronger shift of the K valley to lower energy under tensile strain. Note, that in the exciton picture, the behaviour described above will translate in the corresponding energy shifts of the momentum-bright K-K exciton and the momentum-dark Q-K exciton.

Fig.3b shows a room temperature PL spectrum for the unstrained 2L-WSe₂ placed on a flat GaP substrate. In contrast to what found for the monolayer, the bilayer exhibits a broad spectrum composed of two peaks, attributed to the momentum indirect $E_{Indirect} = 1.55$ eV and momentum direct $E_{Direct} = 1.63$ eV exciton transitions.^{16,67} The corresponding individual peaks obtained from the fitting of the PL spectrum are shown with dashed lines in Fig.3b.

In analogy with the analysis carried out for WSe₂ monolayers, we collected the PL emission of the strained bilayer placed on top of the nano-antennas with different radii. The normalized PL spectra measured for the nano-antennas of different radii are shown in Fig.3c (see also Supplementary Fig.S5). For the strained WSe₂ bilayer, the presence of two transitions leads to a less evident strain-induced shift of the PL spectra. However, by comparing the spectral shape to that of the unstrained case we observe that, as the nano-antenna radius is reduced, the higher energy side of the spectrum shows a consistent shift to lower energies, following an abrupt change of the PL spectrum from that on the flat GaP (dashed red line) to the spectrum measured on a pillar with $r = 500$ nm (yellow). The shift is accompanied with a reduction of the linewidth related to the reduction of the exciton-phonon coupling in

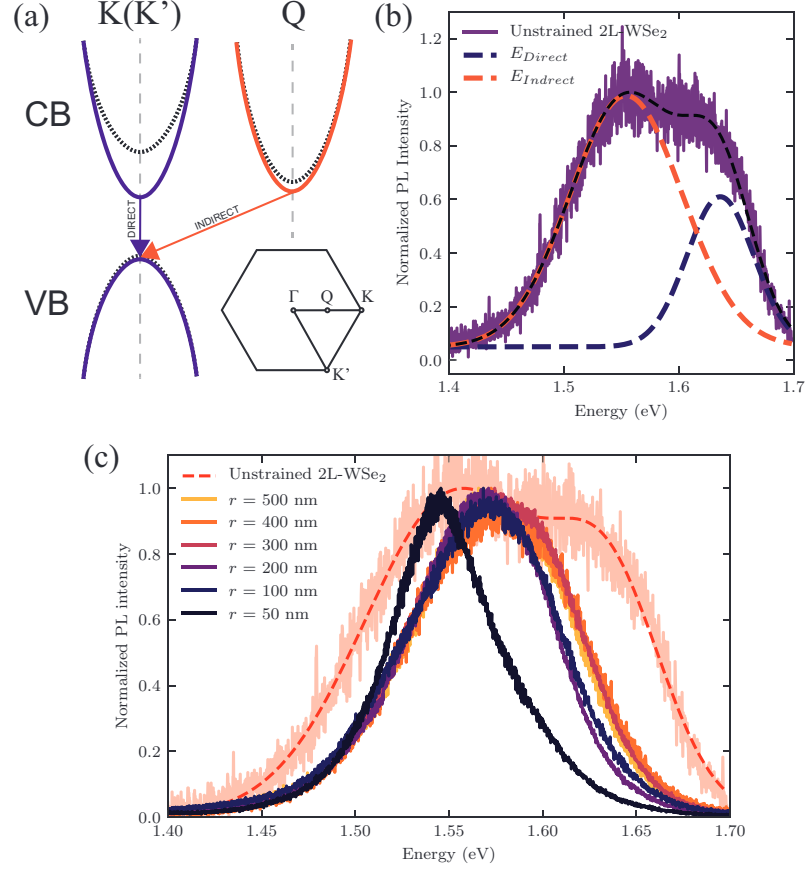


Figure 3: (a) Schematic of the band structure modification in 2L-WSe₂ under tensile strain. The black dashed line shows the case of the unstrained 2L-WSe₂, where the lowest energy radiative recombination occurs as a result of the momentum-indirect $Q \rightarrow K$ transition. Purple (orange) lines show the modification of the $K(Q)$ valley energies under tensile strain. Arrows show momentum-direct (purple) and indirect (orange) transitions giving rise to PL. (b) PL spectrum of unstrained 2L-WSe₂ placed on a planar GaP substrate. Fitting reveals individual PL peaks associated with the indirect ($Q \rightarrow K$, $E_{Indirect}$, orange) and the direct ($K \rightarrow K$, E_{Direct} , purple) transitions. (c) Normalized PL spectra measured for 2L-WSe₂ on top of GaP nano-antennas with different radii and deposited on planar GaP substrate (dashed line).

WSe₂ under strain.⁵⁷ We attribute the red-shift under increasing tensile strain to the reduction in energy of the $K \rightarrow K$ transition, as we observed for the monolayer case. Moreover, the PL lineshape exhibits a further abrupt change when the 2L-WSe₂ is deposited on top of a GaP dimer nano-antenna with $r = 50$ nm. This spectral shape and peak position resemble those reported in Ref.^{65,66} where they were attributed to a transition to the direct bandgap, occurring due to the red-shift of the high-energy peak at E_{Direct} (see also Supplementary

Note V). Our theoretical model predicts strain values $> 3\%$ for 2L-WSe₂ placed on the nano-antennas with $r = 50$ nm (see Supplementary Fig.S2). This value is comparable with the reported threshold for the direct bandgap transition observed in WSe₂ bilayers.⁶⁶

Note, that for the pillars of the same radius, a higher strain is introduced in the bilayer compared with a monolayer, due to the larger rigidity and larger mass of the former. Thus, a stronger bandgap tuning is observed in a bilayer. A similar effect has been reported in suspended 1L and 2L-MoS₂ under the strain introduced by an AFM probe.²⁸

Exciton confinement in the strain-induced potential Controlled nano-scale deformations observed in Fig.1-3 allow the control of exciton motion in 2D semiconductors by means of band structure modification.^{33,34} For WSe₂, the application of tensile strain results in the increase of the valence band edge energy and reduction of the conduction band edge energy at the K point. This effect leads to so-called exciton funnelling,^{33,58} where a strain gradient directs the excitonic population towards the strain-induced potential well. This effect has been proposed to play a role in the population of the single photon emitting centres in WSe₂ at cryogenic temperatures.^{35,36} In order to elucidate the role of the confinement produced by the strain, we probed the spatial dependence of the PL emission of 2L-WSe₂. The experiments are carried out at a cryogenic temperature of 4 K where the effect of the strain-induced confinement is most pronounced.

From our strain topography model, it is possible to calculate the strain-induced potential for the case of the dimer structures (see Supplementary Note II). We find that the strain-induced potential wells are located at the nano-pillar edges, where the tensile strain is maximized.^{33,58} When strain becomes compressive, i.e. where the layer touches the substrate, we observe the presence of potential barriers due to the opposite shift of the band edges, leading to an increase of the bandgap energy. Fig.4a shows the profile of the strained 2L-WSe₂ (dashed line) on top of a dimer nano-antenna with $r = 500$ nm (red squares). The TMD profile shown in the top panel is calculated for a cross section along the x -axis (as defined in Fig.1e), where $x = 0$ is the centre of the dimer gap. We correlate the local de-

formation with the changes in the energy of the conduction band minimum (V_{cb}), calculated numerically for the K valley (see the bottom panel in Fig.4a and Supplementary Note II for details). The minima of V_{cb} are localized at the nano-pillar edges, resulting in a confinement potential wells (shaded areas). For WSe₂ the valence band maximum, V_{vb} , exhibits an increase (decrease) in case of tensile (compressive) strain, also resulting in a confinement for holes, although this effect is weaker compared to conduction band electrons. In such a potential landscape, the exciton population will accumulate in the potential wells at the nano-pillar edges.

Fig.4b shows a reference PL spectrum of 2L-WSe₂ collected at $T = 4$ K on the planar GaP (black) and on a dimer nano-antenna with $r = 500$ nm (orange). The low temperature PL of 2L-WSe₂ is dominated by the low energy broad band between 1.5 and 1.6 eV, relatively weakly dependent on the strain induced by the dimer. Overall the spectrum is characterized by the non-trivial combination of PL from bright and dark states, phonon replicas⁶⁸ and emission of various localized states.⁶⁹ The only part of this broad band that consistently shows dependence on the strain induced by the pillars is the lower side of the spectrum between 1.5 and 1.55 eV, which exhibits higher intensity in the strained WSe₂. One of the reasons for such behaviour could be that the PL in the range 1.55-1.6 eV may originate from the transitions involving the Q valley in the conduction band,⁶⁸ which is weakly sensitive to the strain. On the other hand, we may conclude that the PL in the spectral range of 1.5 to 1.55 eV may arise from the localized exciton states, with the energies following the overall reduction in the direct bandgap by about 45 meV (see details below), or perhaps the optical transitions involving the K valley in the conduction band. However, the complete understanding of this behaviour requires elaborate theory for the optical transitions in bilayer WSe₂ and is beyond the scope of this work.

Despite the very low PL intensity, as expected at low T in WSe₂, we are still able to observe the momentum-direct $K \rightarrow K$ exciton transition for the unstrained WSe₂ on the planar GaP at 1.7 eV (inset Fig.4b). As expected for the direct transition, in the strained

WSe₂ placed on the nano-antenna, the corresponding exciton peak is observed approximately 45 meV lower at 1.655 eV (denoted X). From this energy red-shift we estimate a tensile strain value of $\approx 1\%$, consistent with our theoretical model predictions. As we show in Supplementary Note VI, we observe a similar red-shift in the cryogenic PL of the strained 1L-WSe₂ exciton, also in agreement with our model.

Fig.4c shows a one-dimensional hyper-spectral PL image of 2L-WSe₂ placed on top of four GaP nano-antennas having $r = 500$ nm and the gap size varying between 100 and 150 nm from left to right. The PL image is measured by scanning the collection and excitation spot along the nano-antenna x -axis (see Fig.1e for the axis definition), while on the vertical axis of the figure we report the spectral distribution of the collected PL emission. The increased PL intensity corresponds to the enhanced 2L-WSe₂ PL on top of the dimer nano-antennas, with a negligible signal collected on the flat GaP (dark areas in between).

In the right panel of Fig.4c we zoom in on the direct exciton PL emission in the strained WSe₂ at around 1.655 eV. The exciton PL intensity exhibits a clear localization into two spatially separated maxima. Fig.4d shows the integrated intensity of the exciton PL (in black) clearly highlighting this behaviour. Such two-peaked distribution is also reproduced to some degree for the lowest part of the PL spectrum below ≈ 1.52 eV. This is a consequence of the sensitivity of this part of the spectrum to the induced strain as observed in Fig.4b. We conclude that for the two types of states, exciton relaxation into the strain-induced potential minima is significant.

As seen both in Fig.4c and d, such two-peaked distribution is not replicated clearly for the broad band between 1.55 and 1.6 eV, which is consistent with a weak sensitivity of the involved electronic states to the strain observed in Fig.4b.

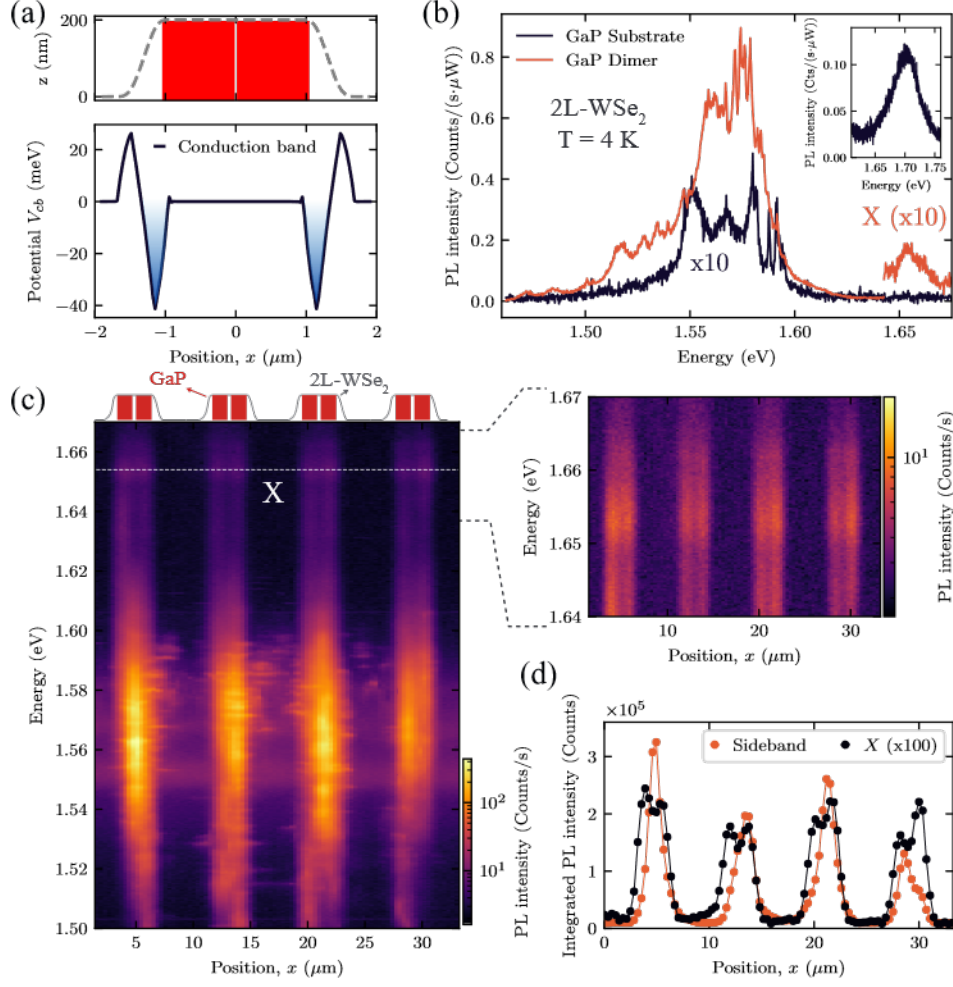


Figure 4: (a) Top panel: cross-section along the x -axis (as in Fig.1e) of the profile for the 2L-WSe₂ (dashed line) on top of a dimer nano-antenna (in red, $h = 200$ nm, $r = 500$ nm). Bottom panel: strain-induced potential (V_{cb}) calculated for the K valley in the conduction band as a function of x . (b) PL spectra measured at $T=4$ K using a laser at 685 nm with a power of 100μ W for 2L-WSe₂ placed on top of the dimer nano-antenna with $r = 500$ nm (orange) and on the planar GaP substrate (black). The spectrum measured for the planar GaP is multiplied by 10. For the orange spectrum, the intralayer exciton PL peak (X) around 1.65 eV is also multiplied by 10. Inset shows intralayer exciton PL measured for 2L-WSe₂ placed on the planar GaP substrate, exhibiting a maximum around 1.7 eV. This PL spectrum is measured in the micro-PL setup used for room temperature measurements (high collection efficiency), using a 532 nm laser with a high power of 1 mW in order to compensate for an extremely low PL intensity of the intralayer exciton. (c) Hyper-spectral image measured at $T=4$ K using a laser at 685 nm with a power of 100μ W showing PL for 2L-WSe₂ deposited on top of four dimer nano-antennas ($r = 500$ nm) separated by $\approx 10 \mu$ m (schematically shown at the top of the panel). As shown in the zoomed-in image, the spatial distribution of the intralayer exciton PL shows a clear localization in two spatially separated PL maxima, as predicted by the potential presented in Fig.4a. (d) Integrated PL intensity as a function of x . The data in black is for the intralayer exciton with integration limits 1.65-1.66 eV (the PL intensity is multiplied by 100), and in orange for the broad PL band with integration limits 1.56-1.58 eV.

Discussion

In summary, we have demonstrated strain-tuning of the electronic band structure in 2D semiconductor WSe₂ by placing the atomic mono- and bilayers on pre-patterned dielectric nano-antennas. Because of the efficient coupling with the optical mode confined at the surface of the nano-antenna, the PL of the strained WSe₂ is enhanced. It can thus be clearly detected with negligible contribution from the PL of the unstrained material, that would normally mask the effect of strain, for example, in the case of the pillars made of SiO₂ or polymers, which were employed previously to induce strain.^{32,36} We therefore can clearly deduce the amount of induced strain from the red-shift in WSe₂ PL spectra at room temperature in agreement with our theory. Moreover, we observe excitons confined into strain-induced potential wells at cryogenic temperature, the presence of which is also predicted by our theoretical model.

The results presented in this work open the way for the use of strain as an additional degree of freedom in engineering of the light-matter interaction in 2D materials, and could find applications for studying 2D excitons in confined potentials, relevant for positioning of strain-induced WSe₂ quantum emitters,^{35,36} as well as for Bose-Einstein condensation of interlayer excitons in TMDs heterostructures.⁷⁰

Additionally, our continuum-mechanical theoretical approach can be expanded to describe the strain distribution and resulting distortion potential for 2D TMDs coupled to a broad range of nano-structures including plasmonic nano-antennas. This opens the way for designing optically active nano-phonic platforms interfaced with strained 2D materials and their heterostructures, with prospects in photodetection, light emission and photovoltaic applications.

Methods

Sample fabrication The GaP nano-antennas are fabricated with a top-down lithography process, as described in Ref.⁵⁶ The monolayers and bilayers of WSe₂ were mechanically

exfoliated from commercially available bulk crystal (HQGraphene) and the layer thickness identified via a PL imaging technique.⁶² The 2D layers are transferred on top of the GaP nano-antennas in a home-built transfer setup, with an all-dry transfer technique.⁷¹

Optical spectroscopy The PL image used in Fig.1d is obtained in a commercial bright-field microscope (LV150N Nikon), with the technique described in Ref.,⁶² where the white light source is used both to image the TMD layers and to excite its PL emission. A 550 nm short-pass filter is placed in the illumination beam path to remove the low energy side of the white light emission spectrum. A high numerical aperture objective (Nikon x100 NA=0.9) is used to direct the light on the sample and for collecting the reflected and emitted light. In the collection path a 600 nm long-pass filter rejects the white light source, while the PL image from the TMD layer is detected with a microscope camera (DS-Vi1, Nikon).

Room temperature optical spectroscopy is performed in a home built micro-PL setup in back reflection geometry. A diode laser with a wavelength of $\lambda_{exc} = 685\text{nm}$ is used as the excitation source and directed into an infinity corrected objective (Mitutoyo 100x NA=0.7), allowing focussing in a $3\text{ }\mu\text{m}$ spot. We use a laser power of $30\text{ }\mu\text{W}$. The sample is placed on a motorized stage (STANDA-8MTF) which allows the automated mapping of the sample surface. The emitted light is collected by the same objective and using free space (no optical fibers) is then coupled to a spectrometer (Princeton Instruments SP2750) equipped with a high-sensitivity liquid nitrogen cooled charge-coupled device (Princeton Instruments PyLoN).

For optical spectroscopy at cryogenic temperature $T \approx 4\text{ K}$, the sample is placed into a microscope stick (attocube systems AG) with a cage structure and a window for optical access. The sample is placed onto piezoelectric nano-positioners (attocube ANP101 models). The cage structure is fitted into an aluminium tube and held under high-vacuum. The tube is then inserted in a liquid helium bath cryostat and an optical breadboard with a micro-PL setup is placed on top of the tube to carry out the optical analysis. PL spectra were excited with the same laser as for room temperature measurements with $\lambda_{exc} = 685\text{nm}$. The incident

power was kept at $100\ \mu\text{W}$, and the excitation spot with a diameter of $3\ \mu\text{m}$ was achieved. The light emitted by the sample is coupled to a single mode optical fibre and detected in the same spectrometer/CCD system employed for the room temperature spectroscopy.

Additional measurements at a cryogenic temperature of $T \approx 10\ \text{K}$ reported in the inset of Fig.4b were carried out in a He flow cryostat using the same setup as was employed for the room temperature PL measurements. The PL was excited with a $532\ \text{nm}$ laser with $1\ \text{mW}$ power and coupled via free space into the spectrometer.

Acknowledgement

L. S. and A. I. T. thank the financial support of the European Graphene Flagship Project under grant agreements 785219, and EPSRC grant EP/S030751/1. L. S., A. I. T., M. B. and G. B. thank the European Union’s Horizon 2020 research and innovation programme under ITN Spin-NANO Marie Skłodowska-Curie grant agreement no. 676108. P. G. Z. and A. I. T. thank the European Union’s Horizon 2020 research and innovation programme under ITN 4PHOTON Marie Skłodowska-Curie grant agreement no. 721394. A. G. and A. I. T. acknowledge funding by EPSRC grant EP/P026850/1. J. C., S. M., S. A. M., and R. S. acknowledge funding by EPSRC (EP/P033369 and EP/M013812). S. A. M. acknowledges the Lee-Lucas Chair in Physics and the Solar Energies go Hybrid (SolTech) programme.

Author contributions

L. S., A. I. T., S. A. M., R. S. conceived the idea of the experiment. L. S. and P. G. Z. fabricated WSe_2 layers and transferred them on the GaP nano-antennas. L. S., P. G. Z. and A. G. carried out microscopy and optical spectroscopy measurements on WSe_2 . J. C. fabricated GaP nano-antennas. S. M., J. C. and R. S. designed GaP nano-antennas. L. S., P. G. Z., A. G. and A. I. T. analysed optical spectroscopy data. M. B. and G. B. developed the theory and carried out simulations for strained WSe_2 . G. B., S. A. M., R. S. and A. I. T. managed various aspects of the project. L. S., M. B. and A. I. T. wrote the manuscript

with contributions from all co-authors. A. I. T. oversaw the whole project.

Supporting Information Available

- Optical resonances of GaP dimer nano-antennas; theoretical modelling of strain topography; Raman spectroscopy of strained 1L-WSe₂, Raw PL spectra from strained WSe₂; PL spectra for strained 2L-WSe₂; Strain-induced exciton red-shift in 1L-WSe₂ at cryogenic temperatures;

References

- (1) Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science* (80-.). **2008**, *321*, 385–388
- (2) Guinea, F.; Katsnelson, M. I.; Geim, A. K. Energy gaps and a zero-field quantum Hall effect in graphene by strain engineering. *Nat. Phys.* **2010**, *6*, 30–33
- (3) Duerloo, K.-A. N.; Ong, M. T.; Reed, E. J. Intrinsic Piezoelectricity in Two-Dimensional Materials. *J. Phys. Chem. Lett.* **2012**, *3*, 2871–2876
- (4) Wu, W.; Wang, L.; Li, Y.; Zhang, F.; Lin, L.; Niu, S.; Chenet, D.; Zhang, X.; Hao, Y.; Heinz, T. F.; Hone, J.; Wang, Z. L. Piezoelectricity of single-atomic-layer MoS₂ for energy conversion and piezotronics. *Nature* **2014**, *514*, 470–474
- (5) Roldán, R.; Castellanos-Gomez, A.; Cappelluti, E.; Guinea, F. Strain engineering in semiconducting two-dimensional crystals. *J. Phys. Condens. Matter* **2015**, *27*, 313201
- (6) Amorim, B.; Cortijo, A.; De Juan, F.; Grushin, A. G.; Guinea, F.; Gutiérrez-Rubio, A.; Ochoa, H.; Parente, V.; Roldán, R.; San-Jose, P.; Schiefele, J.; Sturla, M.; Vozmediano, M. A. Novel effects of strains in graphene and other two dimensional materials. *Phys. Rep.* **2015**, *617*, 1–54

- (7) Dai, Z.; Liu, L.; Zhang, Z. Strain Engineering of 2D Materials: Issues and Opportunities at the Interface. *Adv. Mater.* **2019**, *1805417*, 1805417
- (8) Akinwande, D.; Petrone, N.; Hone, J. Two-dimensional flexible nanoelectronics. *Nat. Commun.* **2014**, *5*, 5678
- (9) Mueller, T.; Malic, E. Exciton physics and device application of two-dimensional transition metal dichalcogenide semiconductors. *npj 2D Mater. Appl.* **2018**, *2*, 29
- (10) Manzeli, S.; Ovchinnikov, D.; Pasquier, D.; Yazyev, O. V.; Kis, A. 2D transition metal dichalcogenides. *Nat. Rev. Mater.* **2017**, *2*
- (11) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically Thin MoS₂ : A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 136805
- (12) Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **2010**, *10*, 1271–1275
- (13) Wang, G.; Chernikov, A.; Glazov, M. M.; Heinz, T. F.; Marie, X.; Amand, T.; Urbaszek, B. Colloquium : Excitons in atomically thin transition metal dichalcogenides. *Rev. Mod. Phys.* **2018**, *90*, 021001
- (14) Xu, X.; Yao, W.; Xiao, D.; Heinz, T. F. Spin and pseudospins in layered transition metal dichalcogenides. *Nat. Phys.* **2014**, *10*, 343–350
- (15) Bertolazzi, S.; Brivio, J.; Kis, A. Stretching and breaking of ultrathin MoS₂. *ACS Nano* **2011**, *5*, 9703–9709
- (16) Yun, W. S.; Han, S. W.; Hong, S. C.; Kim, I. G.; Lee, J. D. Thickness and strain effects on electronic structures of transition metal dichalcogenides: 2H-MX₂ semiconductors (M=Mo,W;X=S,Se,Te). *Phys. Rev. B* **2012**, *85*, 033305
- (17) Johari, P.; Shenoy, V. B. Tuning the Electronic Properties of Semiconducting Transition Metal Dichalcogenides by Applying Mechanical Strains. *ACS Nano* **2012**, *6*, 5449–5456

- (18) Chang, C.-H.; Fan, X.; Lin, S.-H.; Kuo, J.-L. Orbital analysis of electronic structure and phonon dispersion in MoS₂, MoSe₂, WS₂ and WSe₂ monolayers under strain. *Phys. Rev. B* **2013**, *88*, 195420
- (19) Guzman, D. M.; Strachan, A. Role of strain on electronic and mechanical response of semiconducting transition-metal dichalcogenide monolayers: An ab-initio study. *J. Appl. Phys.* **2014**, *115*, 243701
- (20) Kormányos, A.; Burkard, G.; Gmitra, M.; Fabian, J.; Zólyomi, V.; Drummond, N. D.; Fal’ko, V. $k \cdot p$ theory for two-dimensional transition metal dichalcogenide semiconductors. *2D Mater.* **2015**, *2*, 022001
- (21) Conley, H. J.; Wang, B.; Ziegler, J. I.; Haglund, R. F.; Pantelides, S. T.; Bolotin, K. I. Bandgap Engineering of Strained Monolayer and Bilayer MoS₂. *Nano Lett.* **2013**, *13*, 3626–3630
- (22) Castellanos-Gomez, A.; Roldán, R.; Cappelluti, E.; Buscema, M.; Guinea, F.; van der Zant, H. S. J.; Steele, G. A. Local Strain Engineering in Atomically Thin MoS₂. *Nano Lett.* **2013**, *13*, 5361–5366
- (23) Feierabend, M.; Morlet, A.; Berghäuser, G.; Malic, E. Impact of strain on the optical fingerprint of monolayer transition-metal dichalcogenides. *Phys. Rev. B* **2017**, *96*, 045425
- (24) Aslan, O. B.; Deng, M.; Heinz, T. F. Strain tuning of excitons in monolayer WSe₂. *Phys. Rev. B* **2018**, *98*, 115308
- (25) Schmidt, R.; Niehues, I.; Schneider, R.; Drüppel, M.; Deilmann, T.; Rohlfing, M.; de Vasconcellos, S. M.; Castellanos-Gomez, A.; Bratschitsch, R. Reversible uniaxial strain tuning in atomically thin WSe₂. *2D Mater.* **2016**, *3*, 021011

- (26) Tedeschi, D.; Blundo, E.; Felici, M.; Pettinari, G.; Liu, B.; Yildirim, T.; Petroni, E.; Zhang, C.; Zhu, Y.; Sennato, S.; Lu, Y.; Polimeni, A. Controlled Micro/Nanodome Formation in Proton-Irradiated Bulk Transition-Metal Dichalcogenides. *Adv. Mater.* **2019**, *31*, 1903795
- (27) Liu, T.; Liu, S.; Tu, K.-H.; Schmidt, H.; Chu, L.; Xiang, D.; Martin, J.; Eda, G.; Ross, C. A.; Garaj, S. Crested two-dimensional transistors. *Nat. Nanotechnol.* **2019**, *1*, 1
- (28) Manzeli, S.; Allain, A.; Ghadimi, A.; Kis, A. Piezoresistivity and Strain-induced Band Gap Tuning in Atomically Thin MoS₂. *Nano Lett.* **2015**, *15*, 5330–5335
- (29) De Sanctis, A.; Amit, I.; Hepplestone, S. P.; Craciun, M. F.; Russo, S. Strain-engineered inverse charge-funnelling in layered semiconductors. *Nat. Commun.* **2018**, *9*, 1652
- (30) Shin, B. G.; Han, G. H.; Yun, S. J.; Oh, H. M.; Bae, J. J.; Song, Y. J.; Park, C.-Y.; Lee, Y. H. Indirect Bandgap Puddles in Monolayer MoS₂ by Substrate-Induced Local Strain. *Adv. Mater.* **2016**, *28*, 9378–9384
- (31) Blundo, E.; Felici, M.; Yildirim, T.; Pettinari, G.; Tedeschi, D.; Miriametro, A.; Liu, B.; Ma, W.; Lu, Y.; Polimeni, A. Evidence of the direct-to-indirect band gap transition in strained two-dimensional WS₂, MoS₂, and WSe₂. *Phys. Rev. Res.* **2020**, *2*, 012024
- (32) Li, H.; Contryman, A. W.; Qian, X.; Ardakani, S. M.; Gong, Y.; Wang, X.; Weisse, J. M.; Lee, C. H.; Zhao, J.; Ajayan, P. M.; Li, J.; Manoharan, H. C.; Zheng, X. Optoelectronic crystal of artificial atoms in strain-textured molybdenum disulphide. *Nat. Commun.* **2015**, *6*, 7381
- (33) Feng, J.; Qian, X.; Huang, C.-W.; Li, J. Strain-engineered artificial atom as a broad-spectrum solar energy funnel. *Nat. Photonics* **2012**, *6*, 866–872

- (34) San-Jose, P.; Parente, V.; Guinea, F.; Roldán, R.; Prada, E. Inverse Funnel Effect of Excitons in Strained Black Phosphorus. *Phys. Rev. X* **2016**, *6*, 031046
- (35) Branny, A.; Kumar, S.; Proux, R.; Gerardot, B. D. Deterministic strain-induced arrays of quantum emitters in a two-dimensional semiconductor. *Nat. Commun.* **2017**, *8*, 15053
- (36) Palacios-Berraquero, C.; Kara, D. M.; Montblanch, A. R.-P.; Barbone, M.; Latawiec, P.; Yoon, D.; Ott, A. K.; Loncar, M.; Ferrari, A. C.; Atatüre, M. Large-scale quantum-emitter arrays in atomically thin semiconductors. *Nat. Commun.* **2017**, *8*, 15093
- (37) Gant, P.; Huang, P.; Pérez de Lara, D.; Guo, D.; Frisenda, R.; Castellanos-Gomez, A. A strain tunable single-layer MoS₂ photodetector. *Mater. Today* **2019**, *27*, 8–13
- (38) Shiue, R.-J.; Efetov, D. K.; Grosso, G.; Peng, C.; Fong, K. C.; Englund, D. Active 2D materials for on-chip nanophotonics and quantum optics. *Nanophotonics* **2017**, *6*, 1329–1342
- (39) Schuller, J. A.; Barnard, E. S.; Cai, W.; Jun, Y. C.; White, J. S.; Brongersma, M. L. Plasmonics for extreme light concentration and manipulation. *Nat. Mater.* **2010**, *9*, 193–204
- (40) Novotny, L.; van Hulst, N. Antennas for light. *Nat. Photonics* **2011**, *5*, 83–90
- (41) Koenderink, A. F. Single-Photon Nanoantennas. *ACS Photonics* **2017**, *4*, 710–722
- (42) Baranov, D. G.; Wersäll, M.; Cuadra, J.; Antosiewicz, T. J.; Shegai, T. Novel Nanostructures and Materials for Strong Light-Matter Interactions. *ACS Photonics* **2018**, *5*, 24–42
- (43) Sortino, L.; Zotev, P. G.; Mignuzzi, S.; Cambiasso, J.; Schmidt, D.; Genco, A.; Aßmann, M.; Bayer, M.; Maier, S. A.; Sapienza, R.; Tartakovskii, A. I. Enhanced light-

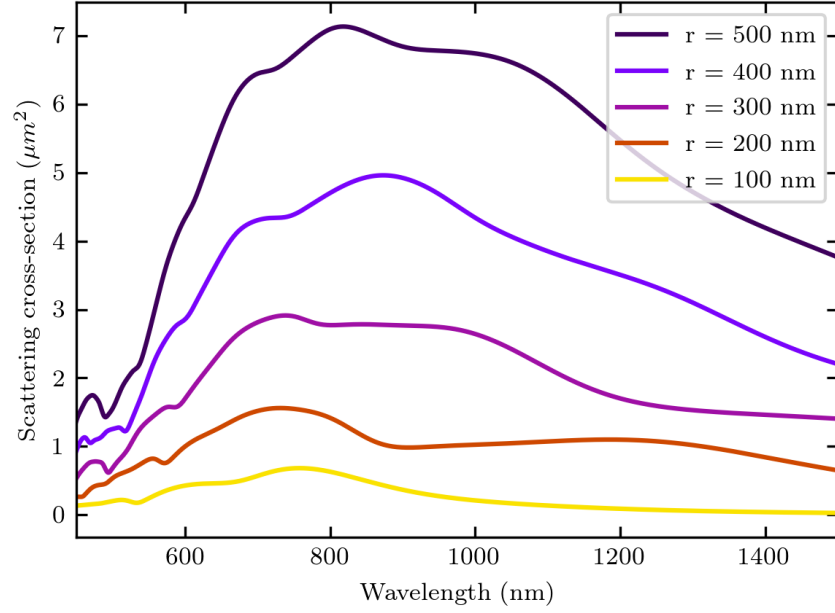
- matter interaction in an atomically thin semiconductor coupled with dielectric nano-antennas. *Nat. Commun.* **2019**, *10*, 5119
- (44) Akselrod, G. M.; Ming, T.; Argyropoulos, C.; Hoang, T. B.; Lin, Y.; Ling, X.; Smith, D. R.; Kong, J.; Mikkelsen, M. H. Leveraging Nanocavity Harmonics for Control of Optical Processes in 2D Semiconductors. *Nano Lett.* **2015**, *15*, 3578–3584
- (45) Wang, Z.; Dong, Z.; Gu, Y.; Chang, Y.-H.; Zhang, L.; Li, L.-J.; Zhao, W.; Eda, G.; Zhang, W.; Grinblat, G.; Maier, S. A.; Yang, J. K. W.; Qiu, C.-W.; Wee, A. T. S. Giant photoluminescence enhancement in tungsten-diselenide-gold plasmonic hybrid structures. *Nat. Commun.* **2016**, *7*, 11283
- (46) Maier, S. A. *Plasmonics: Fundamentals and Applications*; Springer US: New York, NY, 2007
- (47) Giannini, V.; Fernandez-Dominguez, A. I.; Heck, S. C.; Maier, S. A. Plasmonic Nanoantennas: Fundamentals and Their Use in Controlling the Radiative Properties of Nanoemitters. *Chem. Rev.* **2011**, *111*, 3888–3912
- (48) Kuznetsov, A. I.; Miroshnichenko, A. E.; Brongersma, M. L.; Kivshar, Y. S.; Luk'yanchuk, B. Optically resonant dielectric nanostructures. *Science (80-.)*. **2016**, *354*, aag2472
- (49) Cambiasso, J.; König, M.; Cortés, E.; Schlücker, S.; Maier, S. A. Surface-Enhanced Spectroscopies of a Molecular Monolayer in an All-Dielectric Nanoantenna. *ACS Photonics* **2018**, *5*, 1546–1557
- (50) Caldarola, M.; Albella, P.; Cortés, E.; Rahmani, M.; Roschuk, T.; Grinblat, G.; Oulton, R. F.; Bragas, A. V.; Maier, S. A. Non-plasmonic nanoantennas for surface enhanced spectroscopies with ultra-low heat conversion. *Nat. Commun.* **2015**, *6*, 7915

- (51) Kuznetsov, A. I.; Miroshnichenko, A. E.; Fu, Y. H.; Zhang, J.; Luk'yanchuk, B. Magnetic light. *Sci. Rep.* **2012**, *2*, 492
- (52) Cihan, A. F.; Curto, A. G.; Raza, S.; Kik, P. G.; Brongersma, M. L. Silicon Mie resonators for highly directional light emission from monolayer MoS₂. *Nat. Photonics* **2018**, *12*, 284–290
- (53) Hui, Y. Y.; Liu, X.; Jie, W.; Chan, N. Y.; Hao, J.; Hsu, Y.-T.; Li, L.-J.; Guo, W.; Lau, S. P. Exceptional Tunability of Band Energy in a Compressively Strained Trilayer MoS₂ Sheet. *ACS Nano* **2013**, *7*, 7126–7131
- (54) Plechinger, G.; Castellanos-Gomez, A.; Buscema, M.; van der Zant, H. S. J.; Steele, G. A.; Kuc, A.; Heine, T.; Schüller, C.; Korn, T. Control of biaxial strain in single-layer molybdenite using local thermal expansion of the substrate. *2D Mater.* **2015**, *2*, 015006
- (55) Ahn, G. H.; Amani, M.; Rasool, H.; Lien, D. H.; Mastandrea, J. P.; Ager, J. W.; Dubey, M.; Chrzan, D. C.; Minor, A. M.; Javey, A. Strain-engineered growth of two-dimensional materials. *Nat. Commun.* **2017**, *8*, 1–7
- (56) Cambiasso, J.; Grinblat, G.; Li, Y.; Rakovich, A.; Cortés, E.; Maier, S. A. Bridging the Gap between Dielectric Nanophotonics and the Visible Regime with Effectively Lossless Gallium Phosphide Antennas. *Nano Lett.* **2017**, *17*, 1219–1225
- (57) Niehues, I. et al. Strain Control of Exciton-Phonon Coupling in Atomically Thin Semiconductors. *Nano Lett.* **2018**, *18*, 1751–1757
- (58) Brooks, M.; Burkard, G. Theory of strain-induced confinement in transition metal dichalcogenide monolayers. *Phys. Rev. B* **2018**, *97*, 195454
- (59) Landau, L.; Lifshitz, E.; Kosevich, A.; Pitaevski, L. *Theory of Elasticity*; Elsevier, 1986

- (60) Cai, T.; Kim, J.-H.; Yang, Z.; Dutta, S.; Aghaeimeibodi, S.; Waks, E. Radiative Enhancement of Single Quantum Emitters in WSe₂ Monolayers Using Site-Controlled Metallic Nanopillars. *ACS Photonics* **2018**, *5*, 3466–3471
- (61) Luo, Y.; Shepard, G. D.; Ardelean, J. V.; Rhodes, D. A.; Kim, B.; Barmak, K.; Hone, J. C.; Strauf, S. Deterministic coupling of site-controlled quantum emitters in monolayer WSe₂ to plasmonic nanocavities. *Nat. Nanotechnol.* **2018**, *13*, 1137–1142
- (62) Alexeev, E. M.; Catanzaro, A.; Skrypka, O. V.; Nayak, P. K.; Ahn, S.; Pak, S.; Lee, J.; Sohn, J. I.; Novoselov, K. S.; Shin, H. S.; Tartakovskii, A. I. Imaging of Interlayer Coupling in van der Waals Heterostructures Using a Bright-Field Optical Microscope. *Nano Lett.* **2017**, *17*, 5342–5349
- (63) Heeg, S.; Fernandez-Garcia, R.; Oikonomou, A.; Schedin, F.; Narula, R.; Maier, S. A.; Vijayaraghavan, A.; Reich, S. Polarized Plasmonic Enhancement by Au Nanostructures Probed through Raman Scattering of Suspended Graphene. *Nano Lett.* **2013**, *13*, 301–308
- (64) Heeg, S.; Oikonomou, A.; Garcia, R. F.; Maier, S. A.; Vijayaraghavan, A.; Reich, S. Strained graphene as a local probe for plasmon-enhanced Raman scattering by gold nanostructures. *Phys. status solidi - Rapid Res. Lett.* **2013**, *7*, 1067–1070
- (65) Desai, S. B.; Seol, G.; Kang, J. S.; Fang, H.; Battaglia, C.; Kapadia, R.; Ager, J. W.; Guo, J.; Javey, A. Strain-Induced Indirect to Direct Bandgap Transition in Multilayer WSe₂. *Nano Lett.* **2014**, *14*, 4592–4597
- (66) Wu, W.; Wang, J.; Ercius, P.; Wright, N. C.; Leppert-Simenauer, D. M.; Burke, R. A.; Dubey, M.; Dogare, A. M.; Pettes, M. T. Giant Mechano-Optoelectronic Effect in an Atomically Thin Semiconductor. *Nano Lett.* **2018**, *18*, 2351–2357
- (67) Zhao, W.; Ribeiro, R. M.; Toh, M.; Carvalho, A.; Kloc, C.; Castro Neto, A. H.; Eda, G.

- Origin of Indirect Optical Transitions in Few-Layer MoS_2 , WS_2 , and WSe_2 . *Nano Lett.* **2013**, *13*, 5627–5634
- (68) Lindlau, J.; Selig, M.; Neumann, A.; Colombier, L.; Förste, J.; Funk, V.; Förg, M.; Kim, J.; Berghäuser, G.; Taniguchi, T.; Watanabe, K.; Wang, F.; Malic, E.; Högele, A. The role of momentum-dark excitons in the elementary optical response of bilayer WSe_2 . *Nat. Commun.* **2018**, *9*, 2586
- (69) Kumar, S.; Kaczmarczyk, A.; Gerardot, B. D. Strain-Induced Spatial and Spectral Isolation of Quantum Emitters in Mono- and Bilayer WSe_2 . *Nano Lett.* **2015**, *15*, 7567–7573
- (70) Wang, Z.; Rhodes, D. A.; Watanabe, K.; Taniguchi, T.; Hone, J. C.; Shan, J.; Mak, K. F. Evidence of high-temperature exciton condensation in two-dimensional atomic double layers. *Nature* **2019**, *574*, 76–80
- (71) Castellanos-Gomez, A.; Buscema, M.; Molenaar, R.; Singh, V.; Janssen, L.; van der Zant, H. S. J.; Steele, G. A. Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping. *2D Mater.* **2014**, *1*, 011002
- (72) Pearce, A. J.; Mariani, E.; Burkard, G.. Tight-binding approach to strain and curvature in monolayer transition-metal dichalcogenides.. *Phys. Rev. B* **2016**, *94*, 155416

Supplementary note I: optical resonances of GaP dimer nano-antennas



SUPPLEMENTARY FIGURE 1: Simulated scattering cross section of GaP dimer nano-antennas with different radii (height = 200 nm, gap width = 50 nm), excited with a plane wave linearly polarized along the x-axis as defined in Fig.1 of the main text.

Supplementary note II: theoretical modelling of strain topography

The strain topography of stretched transition metal dichalcogenides (TMD) layers is achieved by modelling the out-of-plane displacement relative to the underlying substrate. We applied a continuum-mechanical plate-theory approach, as introduced in Ref.,⁵⁸ with the following reduced form of the Föppl-von Kármán equations, valid for such passively strained low-dimensional systems:⁵⁹

$$D\Delta^2\zeta - P = 0 \quad (1)$$

where P is the pressure the atomic layer experiences, ζ is the function that describes the height profile of the layer,⁵⁸ Δ^2 is the biharmonic operator, given by the square of the Laplacian Δ , and D is the flexural rigidity of the TMD layer defined as:

$$D = \frac{Eh^3}{12(1 - \sigma^2)} \quad (2)$$

here E is the Young's modulus, σ is the Poisson's ratio and h is the TMD layer thickness.

To model the WSe₂ strain topography above the dimer structure, we found a solution to Eq.1. The model of pressure⁵⁸ adopted here, consistent with the microscopy measurements, is the plate model ($P = 0$) with boundary conditions:

$$\zeta_{P=0}(r) = H \quad (3)$$

$$\zeta_{P=0}(r_T) = 0 \quad (4)$$

$$\partial_\rho \zeta_{P=0}|_{r,r_T} = 0 \quad (5)$$

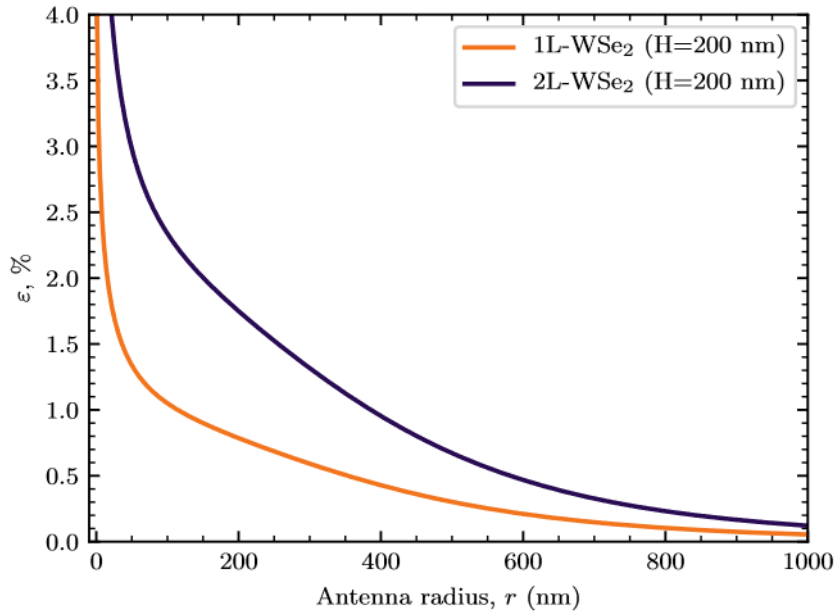
where H is the height of the dimer antenna, r is the nano-pillar radius and r_T is the tenting radius, the distance between the antenna pillars and the point where the WSe₂ layer meets the substrate. We obtain the following analytical solution for the height field, relative to a single pillar, in rotational symmetry:

$$\zeta_{P=0}(\rho) = \frac{H}{(r_T^2 - r^2)^2 - 4r_T^2 r^2 \ln^2 \left[\frac{r_T}{r} \right]} \left\{ 2r_T^2 \ln[r_T] \left(r^2 + 2r^2 \ln \left[\frac{r}{r_T} \right] - \rho^2 \right) \right. \quad (6)$$

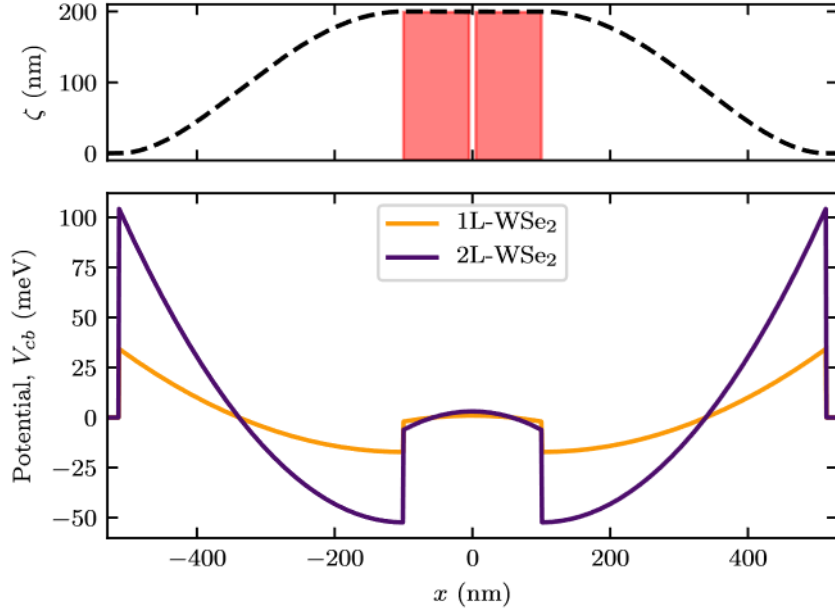
$$\left. + (\rho^2 - r_T^2) (r^2 + 2r^2 \ln[r] - r_T^2) \right. \quad (7)$$

$$\left. + 2 \ln[\rho] \left(\rho^2 (r_T^2 - r^2) + 2r_T^2 r^2 \ln \left[\frac{r_T}{r} \right] \right) \right\} \quad (8)$$

Taking this approximation as a starting point, we obtain a numerically averaged height field over the dimer geometry by taking values of r_T from microscopy measurements, and interpolation in the gap region where the rotational symmetry of the approximate model is



SUPPLEMENTARY FIGURE 2: Uniaxial tensile strain values as a function of the nano-pillar radius, calculated at the topmost edge of the dimer nano-antenna ($H = 200$ nm) for both single and double layer WSe₂.



SUPPLEMENTARY FIGURE 3: Top panel: Height field profile (black dashed line) for a dimer with $H = 200$ nm and $r = 50$ nm, schematically shown in red. Bottom panel: conduction band potential minimum (V_{cb}), calculated for the K(K') point of the Brillouin zone, for both single (1L) and double (2L) layer WSe₂, relative to the height field profile shown in the top panel. The compressive (tensile) strain region is correlated to an increase (decrease) of the potential value.

violated. From a satisfactory model of the height field, the strain component responsible for the band gap renormalization is given by the trace of the strain tensor ε_{ij} , given as:⁷²

$$\mathcal{T} = Tr[\varepsilon_{ij}] = \frac{(2\sigma - 1)h}{1 - \sigma} \Delta\zeta \quad (9)$$

We resolved a relationship between the tensile strain maximum and the nano-pillar radius. Fig.S2 shows the calculated strain values at the topmost edge of a nano-antenna ($H = 200$ nm), as a function of the nano-pillar radius. For both 1L and 2L-WSe₂ we observe an increased strain value as r decreases, with a stronger magnitude for the bilayer. This trend can be explained as the assumed model approaches a deflection of a Dirac-delta like deformation, when $r \rightarrow 0$, giving an undefined pole in the strain value. An increased strain in bilayers is directly related to its larger rigidity (Eq.2).

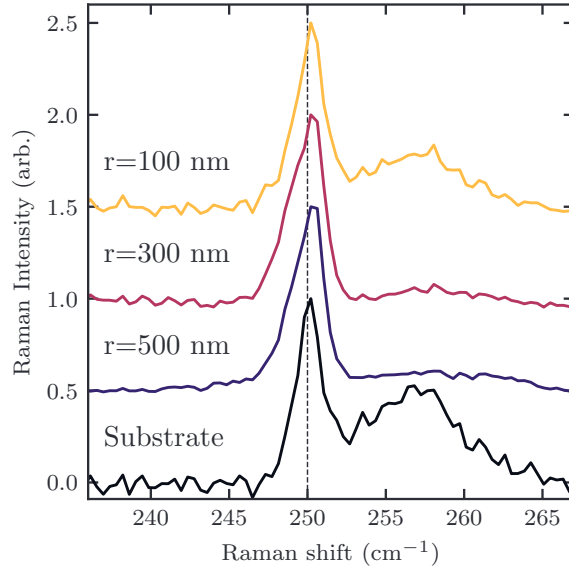
After defining a strain topography, it is possible to calculate a strain-induced deformation potential in the WSe₂ band structure, following a tight-binding approach,^{58,72} as:

$$V = \begin{pmatrix} V_{vb} & 0 \\ 0 & V_{cb} \end{pmatrix} = \begin{pmatrix} \delta_v \mathcal{T} & 0 \\ 0 & \delta_c \mathcal{T} \end{pmatrix} \quad (10)$$

where δ_c and δ_v are the parameters governing the strain response for the conduction (V_{cb}) and valence band (V_{vb}) at the K(K') point, respectively. Fig.S3 shows the calculated conduction band deformation potential, for both 1L and 2L-WSe₂, on a dimer structure with $r = 50$ nm and $H = 200$ nm, along the line connecting the centre of the two nano-pillars. We found a stronger modulation for the bilayer, as expected from the higher strain values shown in Fig.S2. The potential profile is correlated with the local reduction (increase) of WSe₂ bandgap under tensile (compressive) strain. As such, the maximum tensile deformation, located at the nano-antenna edges, corresponds to a decrease in the conduction band minimum. In correspondence with the compressive strain area, where the layers meet the substrate, the bandgap energy is increased resulting in a potential barrier for free excitons.

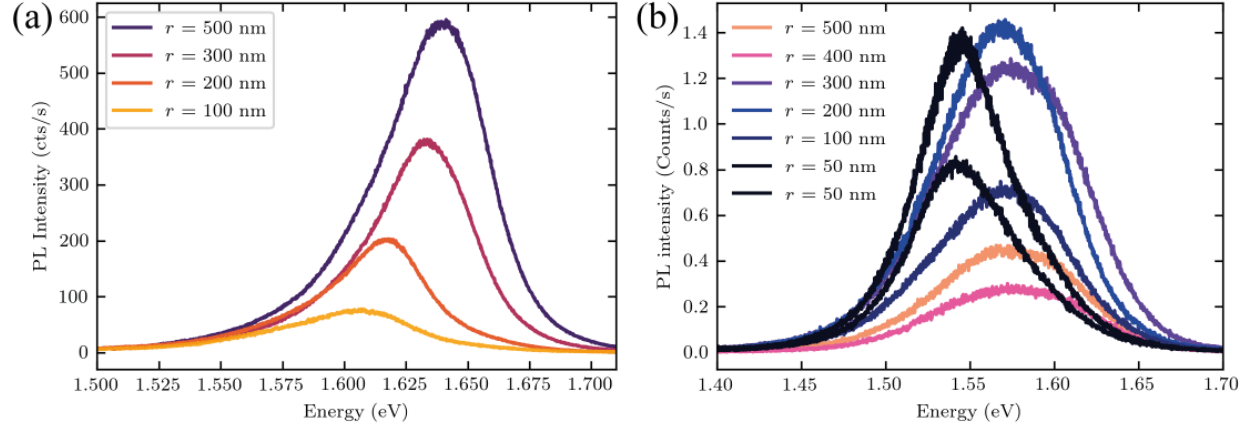
Supplementary note III: Raman spectroscopy of strained 1L-WSe₂

Figure S4 shows the Raman scattering signal from a monolayer of WSe₂ transferred on top of GaP nano-antennas with different radii, compared to the signal from the planar GaP substrate (black). The 1L-WSe₂ peak at 250 cm⁻¹ exhibits a strain-induced shift when deposited on the GaP nano-antennas. The results are consistent with those reported in Ref.⁶⁵ The Raman scattering signal is collected in the setup described in Ref.⁴³



SUPPLEMENTARY FIGURE 4: Raman scattering spectra for 1L-WSe₂ placed on the planar GaP substrate and on different radii nano-antennas. The presence of strain is associated with a shift to higher wavenumber of the main peak at 250 cm⁻¹, corresponding to the $E' + A'_1$ mode. The spectra are normalized and shifted vertically for display.

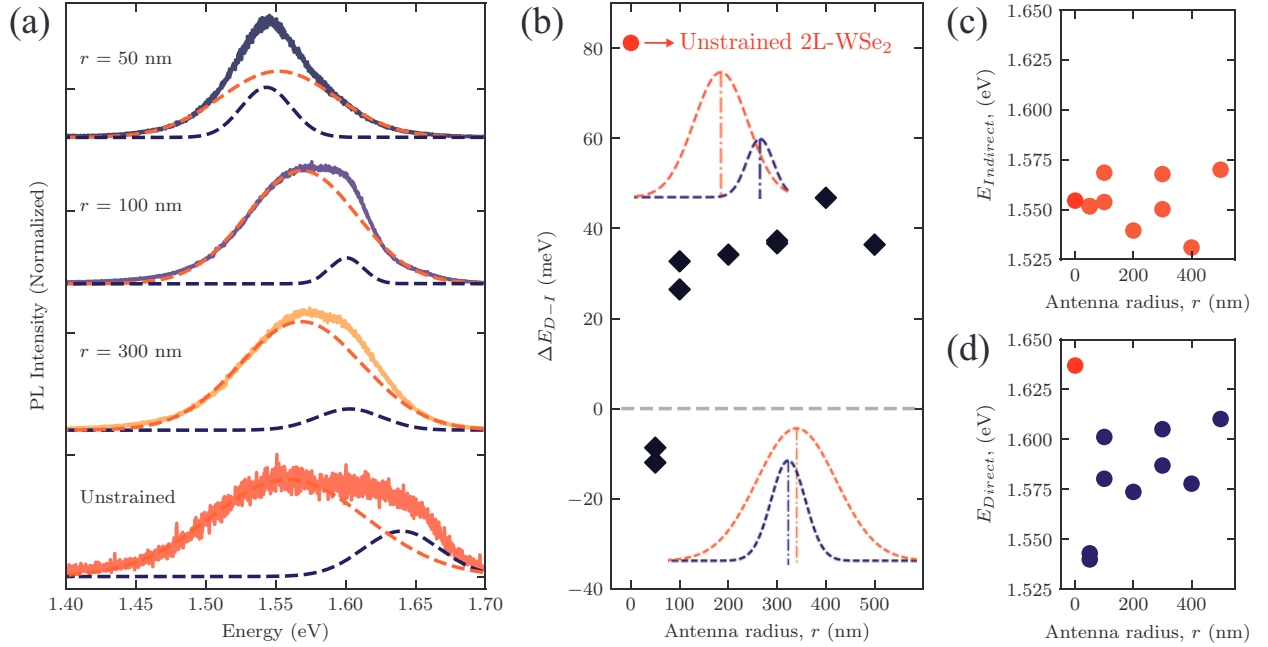
Supplementary note IV: Raw PL spectra from strained WSe₂



SUPPLEMENTARY FIGURE 5: (a) Raw PL spectra for 1L-WSe₂ placed on GaP dimer nano-antennas with different radii. (b) Raw PL spectra for 2L-WSe₂ placed on GaP dimer nano-antennas with different radii. The spectra are collected under the same experimental condition.

Supplementary note V: PL spectra for strained 2L-WSe₂

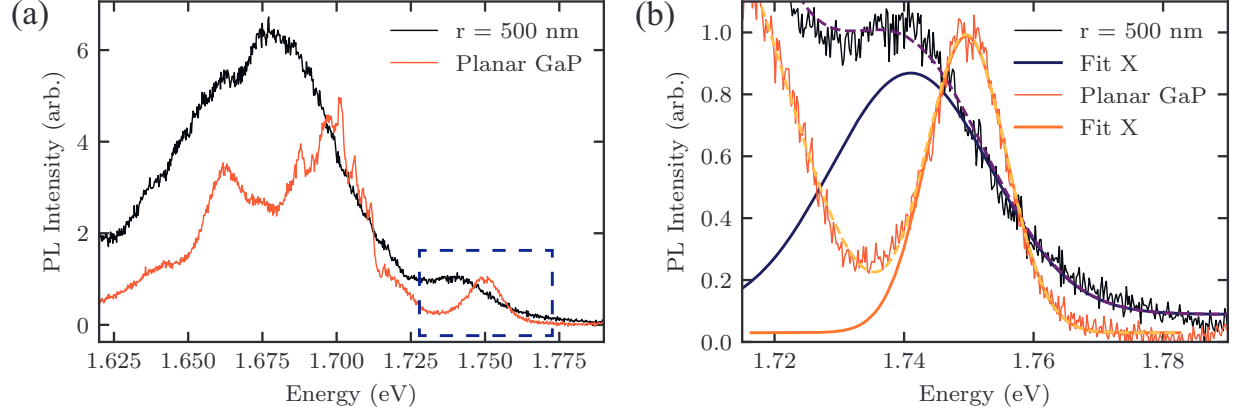
To discriminate the relative role of the competing valleys in the transition to a direct bandgap in strained 2L-WSe₂, we extracted the relative emission peak maxima from the PL spectra (as described in Fig.3 of the main text) when deposited on nano-antennas with different radii (Fig.S6a). The spectra are fitted with two Gaussian functions from which we have extracted their relative energy difference, $\Delta E_{D-I} = E_{Direct} - E_{Indirect}$ (Fig.S6b). For the unstrained bilayer on the planar GaP substrate we found the largest value of $\Delta E_{D-I} \approx 80$ meV. When deposited on the nano-antennas, ΔE_{D-I} exhibits an initial reduction from the unstrained values, further exhibiting a shift of > 30 meV when approaching the nano-antenna with



SUPPLEMENTARY FIGURE 6: (a) 2L-WSe₂ PL emission collected on nano-antenna with different radius. The spectra are fitted with two Gaussian peaks relative to the direct (purple) and indirect (orange) transitions. (b) Energy difference (ΔE_{D-I}) between the direct and indirect peak extracted from the PL emission of 2L-WSe₂ on nanoantennas with different radii. In red the value extracted from unstrained 2L-WSe₂ on planar GaP. The dashed line marks the transition to direct bandgap. (c,d) Direct and indirect peak position (in red for unstrained 2L-WSe₂). No evident change is found in the $E_{Indirect}$ peak (c). In contrast, the E_{Direct} position (d) shows a clear modulation. This effect confirms that a transition to a direct bandgap is caused by the reduction in energy of the $K \rightarrow K$ recombination pathway.

$r = 50$ nm. Figures S6c-d show the position of each peak maxima position, as extracted from the 2L-WSe₂ PL spectra collected on nano-antennas with different radii. As the nano-pillar radius is reduced, thus increasing the strain magnitude as shown in Fig.S2, the $E_{Indirect}$ peak does not exhibit a clear shift in its position when compared to the unstrained case (red circle). On the other hand, we found a large shift of the E_{Direct} , up to a value of approximately 100 meV from the unstrained case. This behaviour confirms the predominant role of the E_{Direct} peak in the indirect-to-direct bandgap transition in 2L-WSe₂ under strain.

Supplementary note VI: Strain-induced exciton red-shift in 1L-WSe₂ at cryogenic temperatures



SUPPLEMENTARY FIGURE 7: (a) PL emission of 1L-WSe₂, collected at T=4 K, on the planar GaP substrate (orange) and on a $r = 500$ nm dimer nano-antenna (black). The spectra are normalized to the intensity of the direct exciton emission peak (dashed line box). (b) Gaussian fit of the direct exciton peak for both spectra shown in Fig.S7a (cumulative fit shown with the dashed line). A red-shift of ≈ 10 meV is observed when on top of the GaP nano-antenna with $r = 500$ nm, consistent with the values extracted at room temperature and with the prediction of our theoretical model.

Graphical TOC Entry

