

Strain Induced Indirect to Direct Bandgap Transition in Multilayer WSe₂

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Supporting Information

Sample preparation method:

WSe₂ (2dsemiconductors.com) was mechanically exfoliated using the adhesive tape method onto 260 nm SiO₂/Si substrate (SVM wafers). The chips were mapped to find the flakes of desired thickness using an optical microscope based on the color and contrast of the flakes, which is determined by the thickness of the underlying oxide (260 nm) and the refractive index of WSe₂. The flakes were then transferred by a dry transfer technique ¹ using PMMA (MicroChem) as the transfer medium, onto a clear and flexible PETG substrate of 1.5 mm thickness. The samples were subsequently annealed at 125° C for 5 minutes so that the flake and PMMA handling medium stick to the PETG. The partial thermoforming /softening of the PETG at the annealing temperature helps clamp the flake along with the PMMA enabling the application of large strain.

Strain Calculation and MoS₂ internal reference:

The bent PETG substrate is approximated as a circular arc for the purpose of strain calculation. A snapshot of the bent PETG is taken at each strain condition and then the parameters ' θ ' and ' a ' as shown in Fig. 1a are extracted. The strain at the top surface of the PETG is given by $\varepsilon = \frac{\tau}{2R}$ where τ is the thickness of the PETG and R is the radius of the bent PETG. From geometry $R = \frac{a}{\sin\theta}$ which gives $\varepsilon = \frac{\tau \sin\theta}{2a}$. The computed strain is valid for low angles of ' θ '. At large ' θ ' the circular arc approximation fails and the maximum strain is $\sim 20\%$ higher². For this work, all strain values are computed using the circular arc approximation. The strain computed is also compared with strain calculated from a MoS₂ internal reference flake which is discussed in Fig. S1 in more detail.

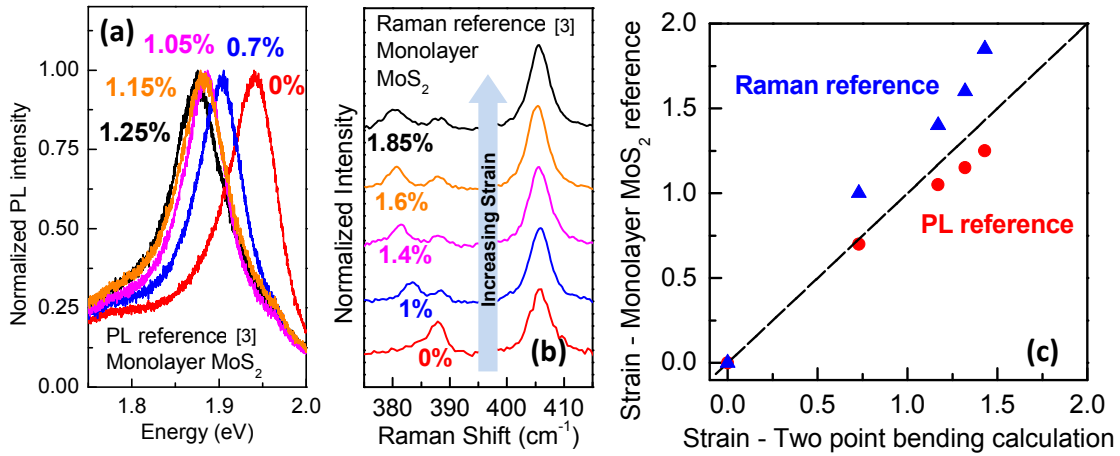


Figure S1: (a) PL spectra for monolayer MoS₂ for varying strain. The shift in the PL peak is used to calculate strain from reference³. The absolute peak value is different from that in ref.³ possibly due to substrate effects (Reference³ used polycarbonate whereas we use PETG). (b) Raman spectra for monolayer MoS₂ for varying strain. Again the shift in the Raman peak is used to compute strain from reference³. (c) The strain from the PL and Raman references in (a) and

(b) is plotted versus the strain computed for the same samples from our own two-point bending calculation showing an almost 1:1 correlation.

Local Strain effects and reversibility of strain:

The Raman and PL measurements over multiple spots on a flake show that small local variations in strain exist on a flake even at zero strain. The local strain effects can be due to multiple reasons such as existing defects, ripples, folds or edges in the flake. In addition small strain can also be induced by thicker adjacent flakes or during the processing of the sample. Multiple spots on a flake were measured and representative data discussed in this work represents the modal trends seen at each strain. A PL line scan on a bilayer sample also shows that local strain variations are over a much larger scale than the spot size of the laser.

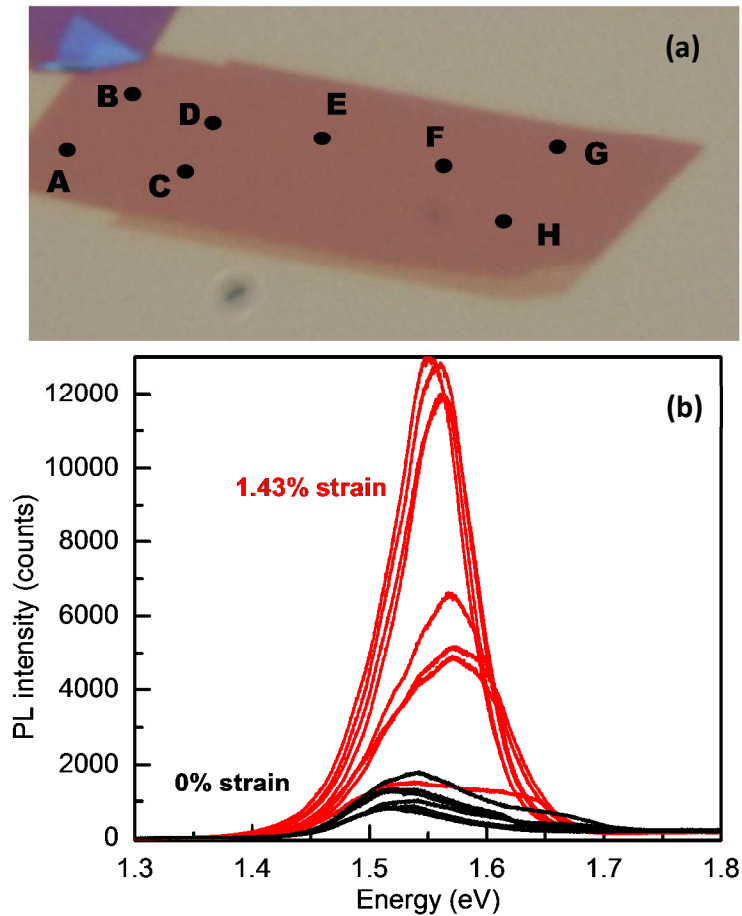


Figure S2: (a) Optical image of bilayer WSe₂ flake showing the spots where PL and Raman spectra are measured. (b) PL spectra for different spots at a given strain indicating the variation in PL due to local strain effects.

Repeated straining experiments with PETG samples were also performed to check the reversibility of strain application. This is important so as to verify that the flake does not slip on the substrate and the strain measured is actually the strain imparted to the flake. The reversibility in trends for a bilayer sample were seen up to a strain of $\sim 1.04\%$. For very large strain, the PETG enters the plastic regime and cannot return to its original unbent shape.

Density functional theory analysis of WSe₂ under uniaxial tensile strain:

Heyd-Scuseria-Ernzerhof (HSE) exchange correlation potential with spin orbit coupling was used to model the electronic band structure for WSe₂. An ultra-soft PAW pseudo-potential with semi-core electrons and a cut-off energy of 400eV for the plane waves was used. For strained WSe₂, structure relaxation was first performed to determine the relaxed atomistic structure in the presence of uniaxial strain, and the band structure in the presence of strain was subsequently calculated. Structural relaxation is achieved by minimizing the energy with a tolerance of 1 meV (for total energy in the range of 44-45eV). Fig. S3 schematically represents the direction of application of strain in the DFT calculations and the reciprocal space of WSe₂.

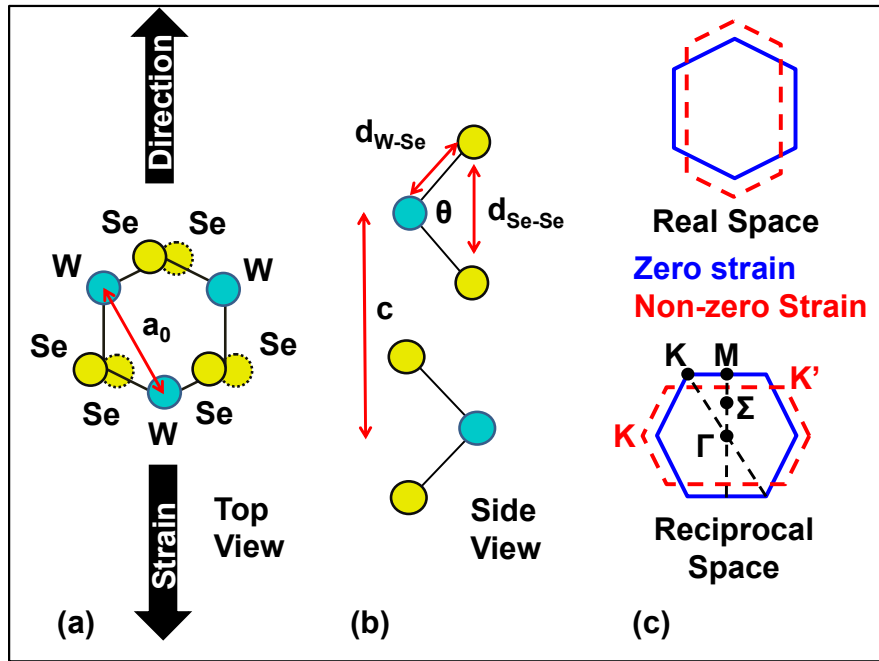


Figure S3: (a) Top view of WSe₂ showing direction of strain (b) Side view of WSe₂ (c) Real and reciprocal space of WSe₂ with and without strain. Reciprocal space shows the K, M, Σ and Γ points.

We see that the crystal lattice and the reciprocal space get stretched when strain is applied. For monolayer WSe₂ as strain is applied the intra-layer Se-Se distance decreases;

whereas for bilayer WSe₂ the Se-Se intra-layer and inter-layer distances decreases whereas the W-Se bond length at the outer Se increases. The degeneracy of the 6 K points is however maintained because the positions of the K, M, Σ , etc. points may have changed, but the E-*k* relation along two different directions say K- Γ and K'- Γ (Fig. S3c) will still be the same because the reciprocal lattice vectors have also changed.

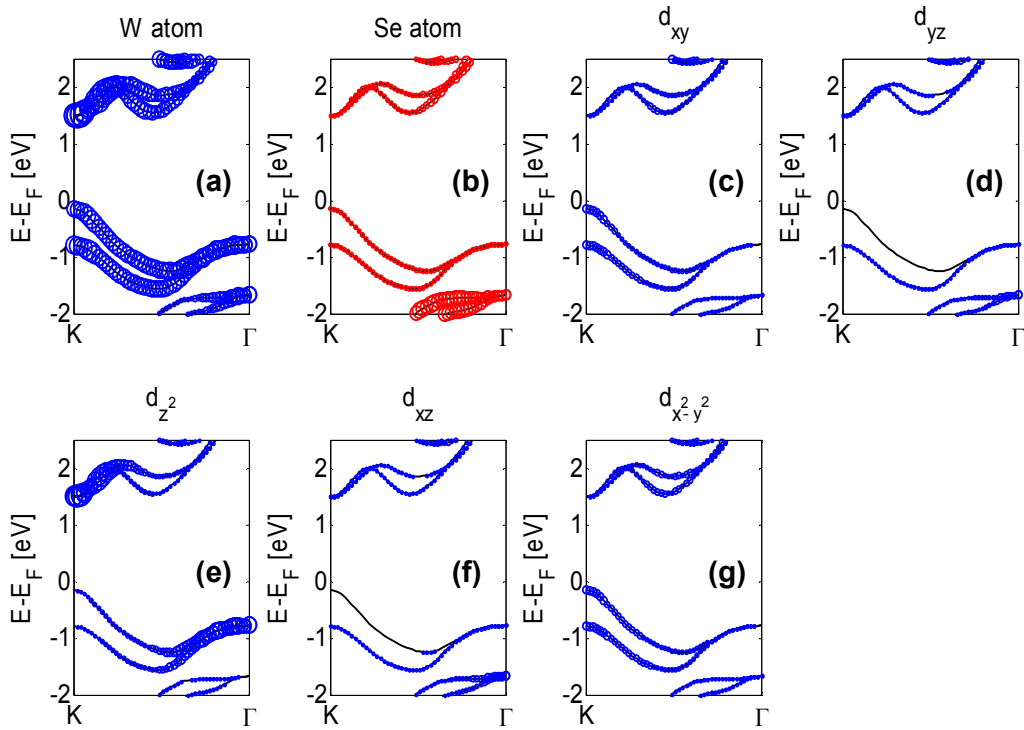


Figure S4: Electronic band structure for unstrained monolayer WSe₂ from HSE-DFT simulations showing the relative contribution of different orbitals to the energy bands, which is directly proportional to the size of the circles on the curves. (a) W atom orbital and (b) Se atom orbital contributions. (c-g) Different W orbital contributions to the energy bands.

Fig. S4a and Fig. S4b clearly illustrate that the W atom orbitals dominantly contribute to the energy bands near the conduction band (CB) minima and the valence band (VB) maxima. From Fig. S4c to Fig. S4g we also understand that the contribution of the W d_{z^2} orbital to the CB

minima at the K point is maximum. The above observations are found to be true for bilayer WSe_2 as well from the DFT calculations. Thus change of the interlayer W-W distance in strained bilayer WSe_2 and hence the orbital overlap for the d_{z^2} orbitals affects the CB minima at the K point drastically and leads to an indirect to direct bandgap transition as explained in Fig. 2b in the main text.

Effect of uniaxial tensile strain on monolayer WSe₂:

Monolayer WSe₂ PL spectra at different strain in Fig. 4a clearly show an increase in PL intensity with increasing strain. Also peak shifts and FWHM becomes narrower. For no strain case the PL peak is at 1.7eV (shifted from 1.65eV when on SiO₂) and also shows a significant red tail. This can be possibly due to substrate and excitonic effects in WSe₂. Raman spectra at different strain for monolayer WSe₂ in Fig. 4b show peak splitting of the E_{2g}¹ mode indicating that strain is applied on the flake.

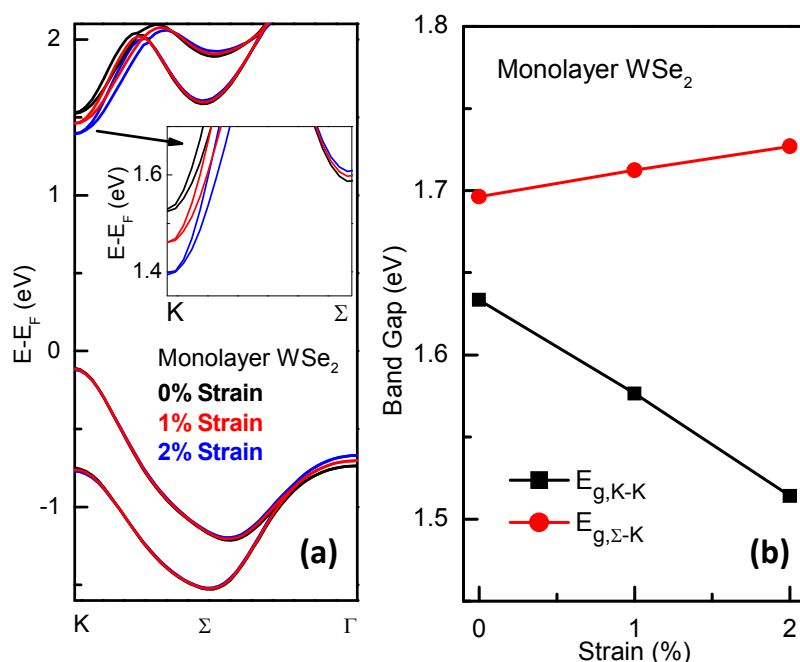


Figure S5: (a) Electronic band structure for monolayer WSe₂ from HSE-DFT simulations showing the bandstructure w and w/o strain. CB minima at K point moves down drastically indicating that monolayer WSe₂ remains direct bandgap even under tensile strain and the difference between the indirect and the direct valleys increases further. (b) Indirect and direct bandgap values obtained from HSE-DFT simulations for monolayer WSe₂.

Raman and PL spectra at different strain for bulk WSe₂:

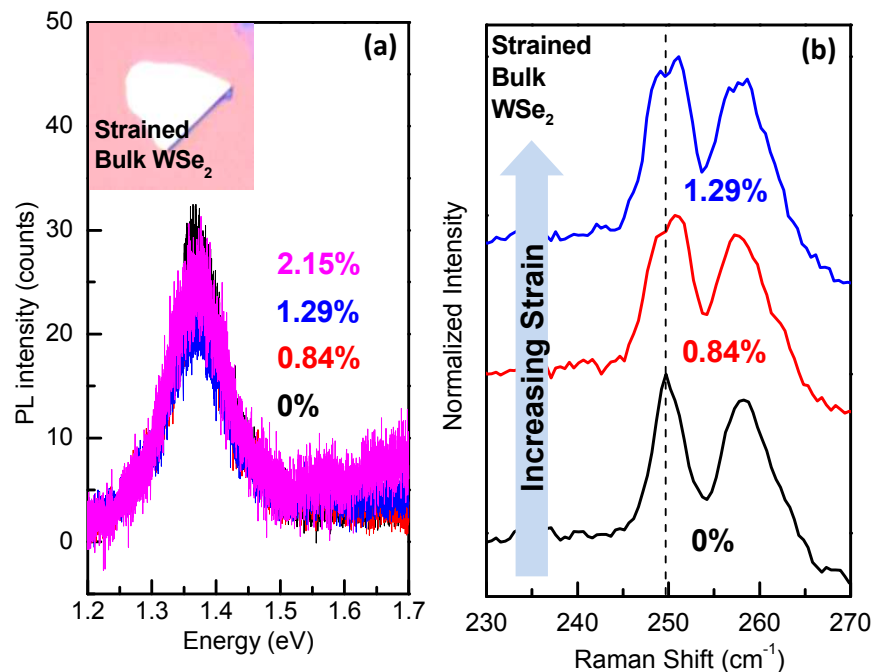


Figure S6: (a) PL and (b) Raman spectra at different strain for bulk WSe₂. Inset shows corresponding flake. Peak splitting seen in all spectra at non-zero strain. PL spectra at different strain for bulk WSe₂ show no change in PL consistent with the fact that for bulk WSe₂ the direct and indirect bandgap difference is very large ($\sim 200\text{meV}$)⁴, thus requiring huge strain for a crossover.

G_0W_0 calculation approach:

In the following GW quasi-particle (QP) calculation, non-self-consistent G_0W_0 was used to reduce the computational cost⁵. Same atomistic relaxed structure was used as in the main text. HSE exchange-correlation functional was used to obtain wave functions for the GW calculation. Although this step is not essential, this method has been suggested to improve agreement with experiments⁶. The Brillouin zone sampled with a $6 \times 6 \times 1$ k-point mesh. The band-structure was Wannier interpolated using the WANNIER90 program⁷. From the figure S7a, ~ 0.65 eV shift of CBM as regard to the valence band can be observed. In figure S7b, splitting the valence bands due to spin orbital coupling is shown.

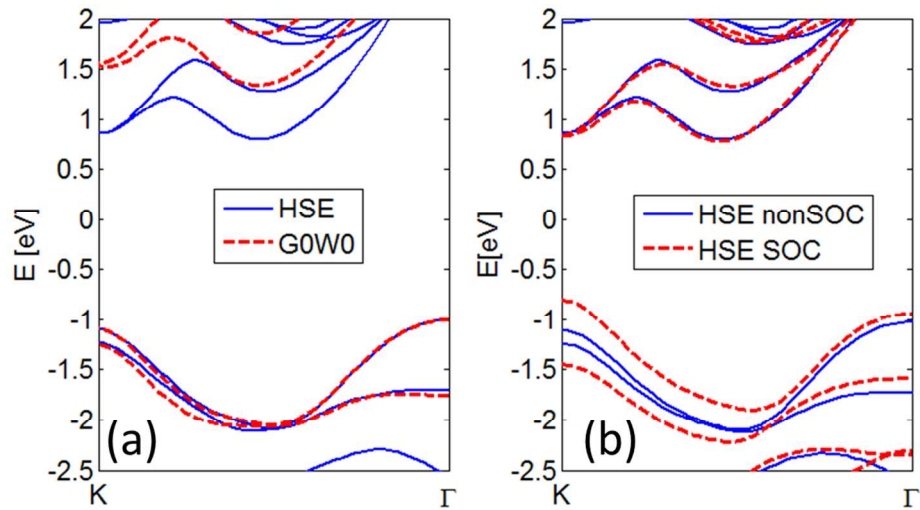


Figure S7: (a) Comparison of Wannier interpolated HSE-DFT and G_0W_0 calculation. SOC is not considered and no strain is applied. (b) Comparison of spin orbital coupling (SOC) effect in HSE-DFT calculation. Band splitting in the K point of the valence band can be observed.

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