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Supporting information

Structural, Spectroscopic, and Excitonic Dynamic Characterisation in atomically thin Yb³⁺ -doped MoS₂, fabricated by femtosecond pulsed laser deposition

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Raman Spectroscopy:

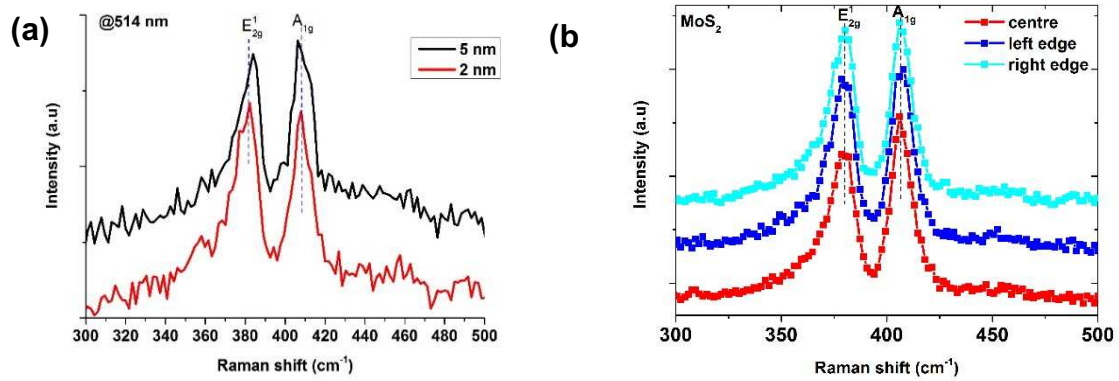
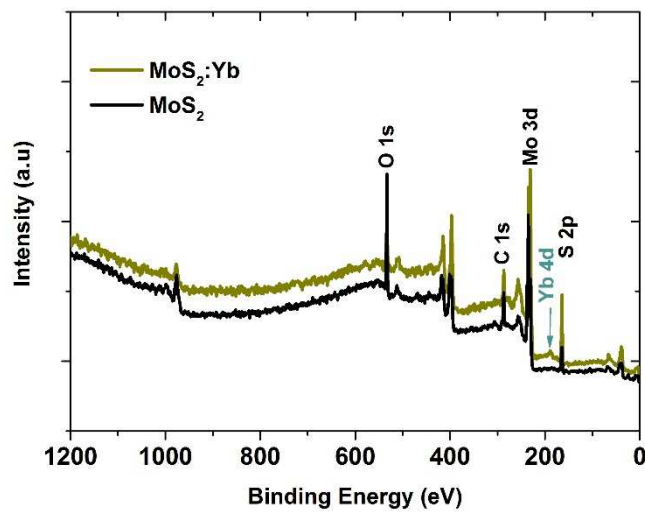


Figure S1: Raman spectra of MoS_2 at excitation wavelength 514 nm: (a) thickness dependent, (b) uniform film thickness measurements.

X-Ray Photoelectron Spectroscopy (XPS):

(a)



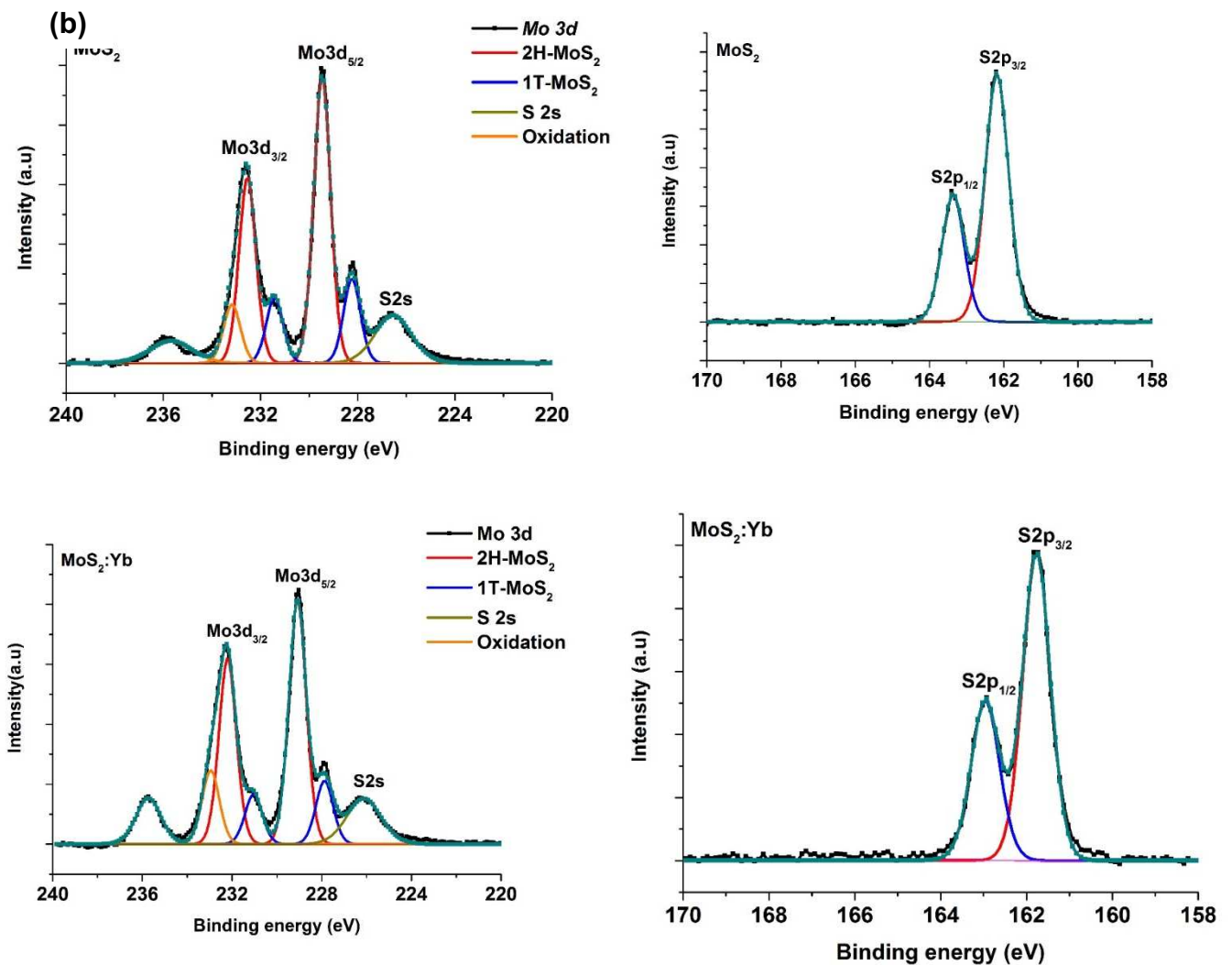


Figure S2: XPS of MoS₂: (a) General scan spectra of undoped and Yb³⁺ doped MoS₂, (b) Comparison of Molybdenum (Mo) and Sulfur (S) core level XPS data for undoped and Yb³⁺-ion doped MoS₂ films.

The chemical composition and doping were estimated by using X-ray photoelectron spectroscopy (XPS). Figure S2 a-e shows the survey scan, Mo 3d, S2s and S2p regions of the undoped and Yb doped MoS₂ samples. Figure S2 (a) shows the comparison of the general scan spectra of MoS₂ and doped MoS₂. Figure S2 (b) shows the comparison of XPS Mo3d core level spectra of MoS₂ and Yb-doped MoS₂. It is observed that the core level spectra of Mo and S in the MoS₂:Yb sample present a uniform shift towards the lower binding energies by ~0.3-0.4 eV with respect to the

peak position of 2H-MoS₂ of undoped MoS₂. Such a shift in binding energy indicates the change in the chemical microenvironment of doped samples, the Fermi level shift is a clear indication of doping of Yb into Mo lattice. The Mo 3d spectra consist of peaks at around 229.47 eV and 232.54 eV corresponding to Mo⁴⁺3d_{5/2} and Mo⁴⁺3d_{3/2} spin orbital doublet associated with 2H-MoS₂ phase, respectively. Figure S2b shows the deconvolution of Mo3d spectra of undoped MoS₂ film. The deconvoluted Mo3d spectra of undoped MoS₂ reveal additional peaks which are located at 228.23 eV and 231.44 eV ascribed to 1T-MoS₂ phase, and peaks at 233.18 eV and 235.80 eV associated with the oxidation state. Similarly, the deconvoluted S2p spectra consist of peaks at around 162.19 eV and 163.38 eV corresponding to S 2p_{3/2} and S 2p_{1/2} in undoped MoS₂ film showed in Figure S2 c. Figure S2 d and Figure S2 e show the deconvolution of Mo3d and S 2p of Yb doped MoS₂ films. These films show four distinct features; peaks at 229.05 eV and 232.20 eV corresponding to Mo⁴⁺3d_{5/2} and Mo⁴⁺3d_{3/2} components of 2H-MoS₂, peaks at 227.88 eV and 231.03 eV ascribed to 1T-MoS₂, and peaks at 232.94 eV and 235.67 eV associated with the oxidation states. The deconvoluted S 2p valence spectra (Figure S2 e) of doped MoS₂ consist of doublet peaks at around 161.76 eV and 162.94 eV corresponding to S 2p_{3/2} and S 2p_{1/2}, respectively. When the films were compared with respect to other, the peaks shifted to lower binding energies in Yb doped MoS₂ than in doped MoS₂. The shift may be attributed to the switch from n-type to p-type conductivity with Yb doping. In order to confirm the type of doping, we need further characterizations of the films. [1-3].

Table S1: Comparison of Mo and S core level binding energy values of undoped and Yb³⁺ doped MoS₂ films.

	2H-MoS ₂ BE, eV	1T-MoS ₂ BE, eV	1T -MoS ₂ BE, eV	S2s BE, eV	S2p3/2 BE, eV	S2p1/2 BE, eV
MoS ₂	Mo3d5/2: 229.47 Mo3d3/2: 232.54	Mo3d5/2: 228.23 Mo3d3/2: 231.44	Mo3d5/2: 233.18 Mo3d3/2: 235.80	226.55	162.19	163.38
MoS ₂ :Yb	Mo3d5/2: 229.05 Mo3d3/2: 232.20	Mo3d5/2: 227.88 Mo3d3/2: 231.03	Mo3d5/2: 232.94 Mo3d3/2: 235.67	226.13	161.76	162.94

Table S2: A comparison of the calculated lattice parameters and relative energies of the 2H and 1T allotropes of MoS₂.

MoS ₂ (bulk)	Space group Crystal system	a (Å)	c (Å)	Mo-S (Å)	ΔE (kJ/ mol.fu) (kJ/mol.atom)
2H	P6 ₃ /mmc Hexagonal	3.1587 (+0.1%)	12.0872 (- 1.4%)	2.401	0 0
1T	P-3m Trigonal	3.1957 (+0.2%)	5.6432 (-5.1%)	2.418	+76.1 +25.4

Band structure calculation (Hybrid functional):

The electronic structure of molybdenum disulfide (MoS₂) was analysed through the first principles calculations using density functional theory (DFT) using CASTEP code. DFT is known to significantly underestimate the bandgap in materials; therefore we have used a recent computationally intensive hybrid functional (HSE06) code, which is able to predict the bandgap accurately. Bulk MoS₂ was geometry optimised (dispersion corrected TS-PBE functional) giving a=3.159 Å (~0.1%) and c=12.071 Å (~1.8%). A monolayer of MoS₂ was modelled using a supercell with an interplanar (vacuum) distance of 15 Å to avoid interactions between adjacent sheets. DFT calculations accurately predict the expected increase in the bandgap from bulk MoS₂ (1.26 eV indirect) to monolayer MoS₂ (~2.27 eV direct). Indirect bandgap of monolayer

MoS₂ lies between point Γ to Γ -K in first Brillouin zone, while the direct bandgap lies in point-K. The indirect and direct bandgap transition observed in MoS₂ when shifted from bulk to monolayer is due to quantum confinement effects [4].

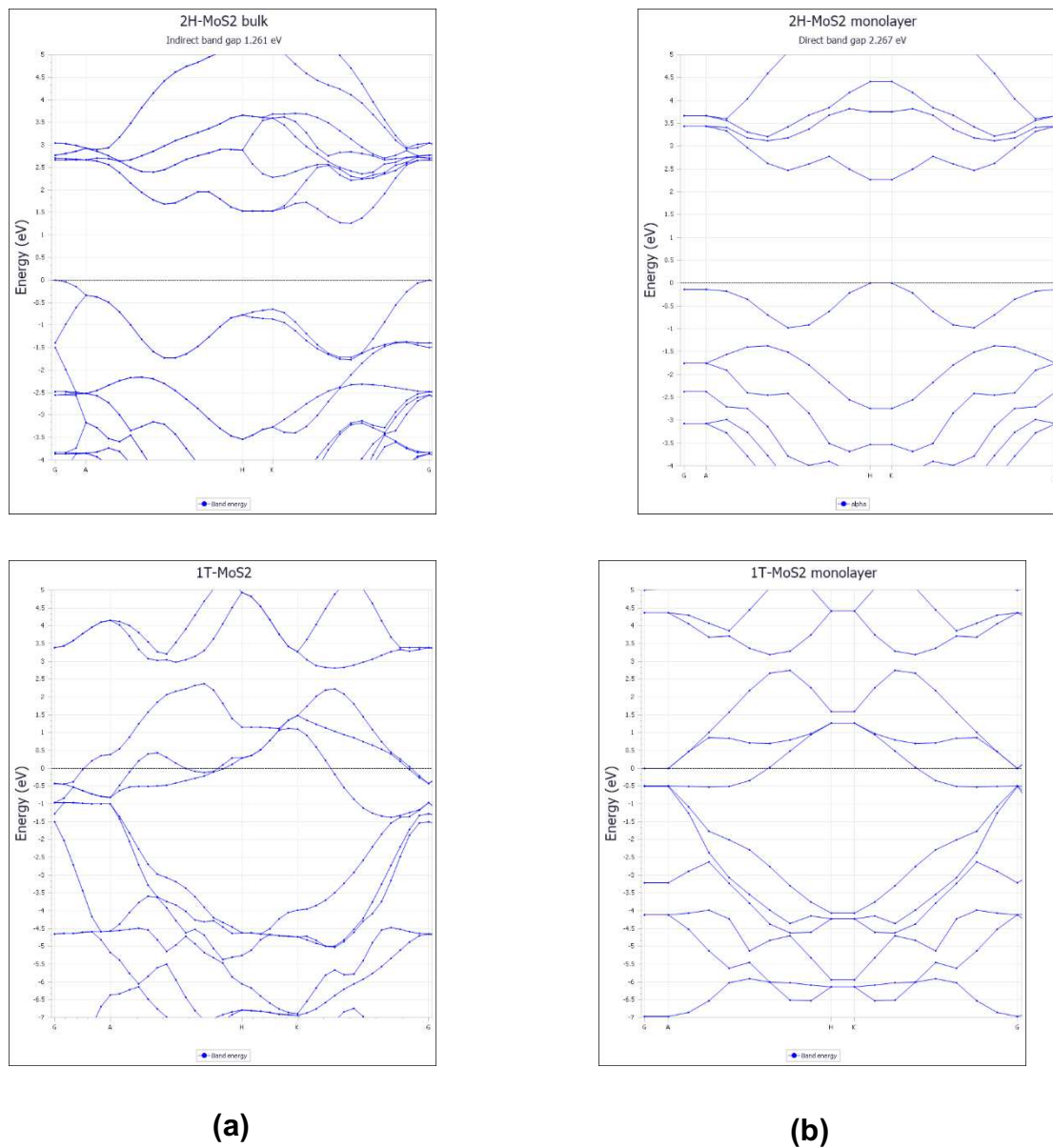


Figure S3: DFT band structure calculations using hybrid functional code, (a) and (b) electronic band structure diagram of bulk and monolayer MoS₂.

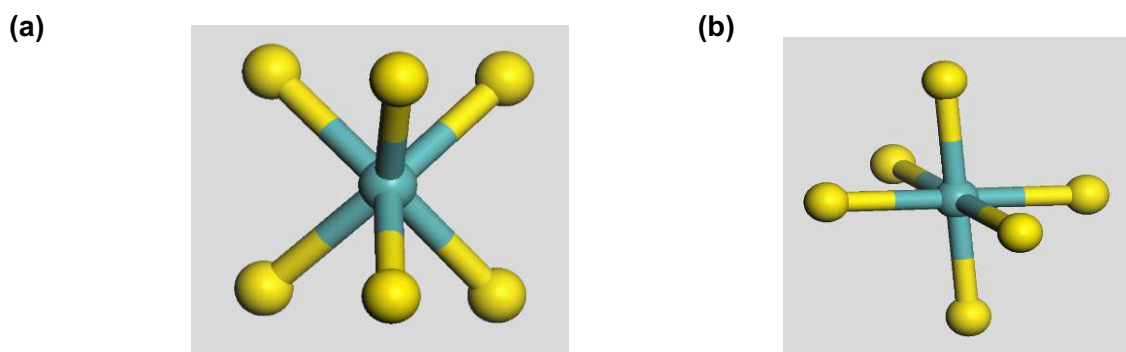


Figure S4: The DFT modelled 2H MoS₂ structure, showing (a) trigonal prism, and b) metastable octahedral 1T co-ordination.

Nonlinear Z-scan:

To measure the nonlinear optical response of the thin films, we have employed a conventional open-aperture Z-scan setup which measures the total transmittance as a function of incident laser intensity. In our Z-scan experiment, 120 fs pulses from a Ti-Sapphire amplifier was used to excite the sample. The low repetition rate was kept at 1 KHz. The beam was focused by a 20 cm focal length lens, and the sample was moved along the z axis of the beam by using a computer controlled translation stage. The Rayleigh length (Z_0) and the beam waist in our experiment were 1.7 mm and ~ 19 μm , respectively.

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