

Twisted Molybdenum Disulfide to Catalyse H₂ Production

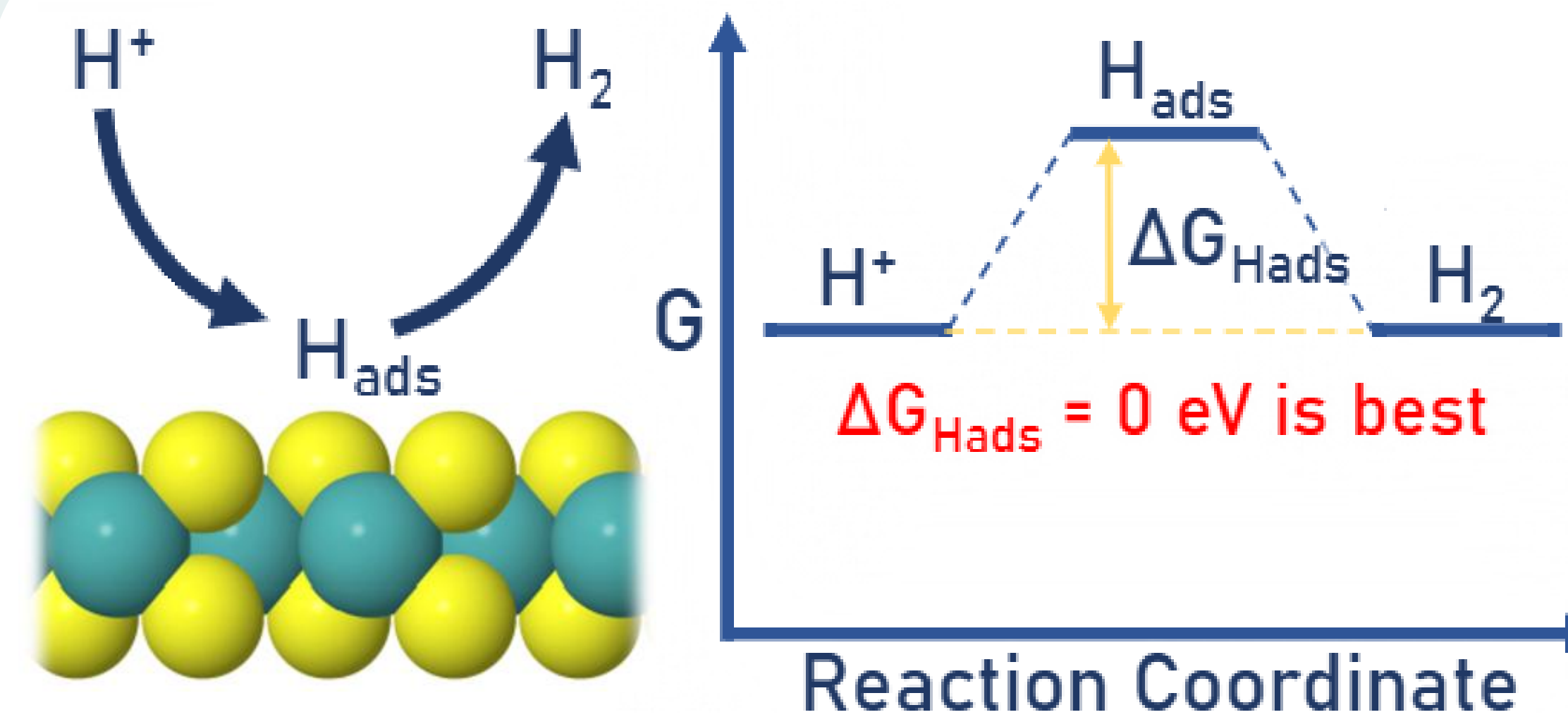
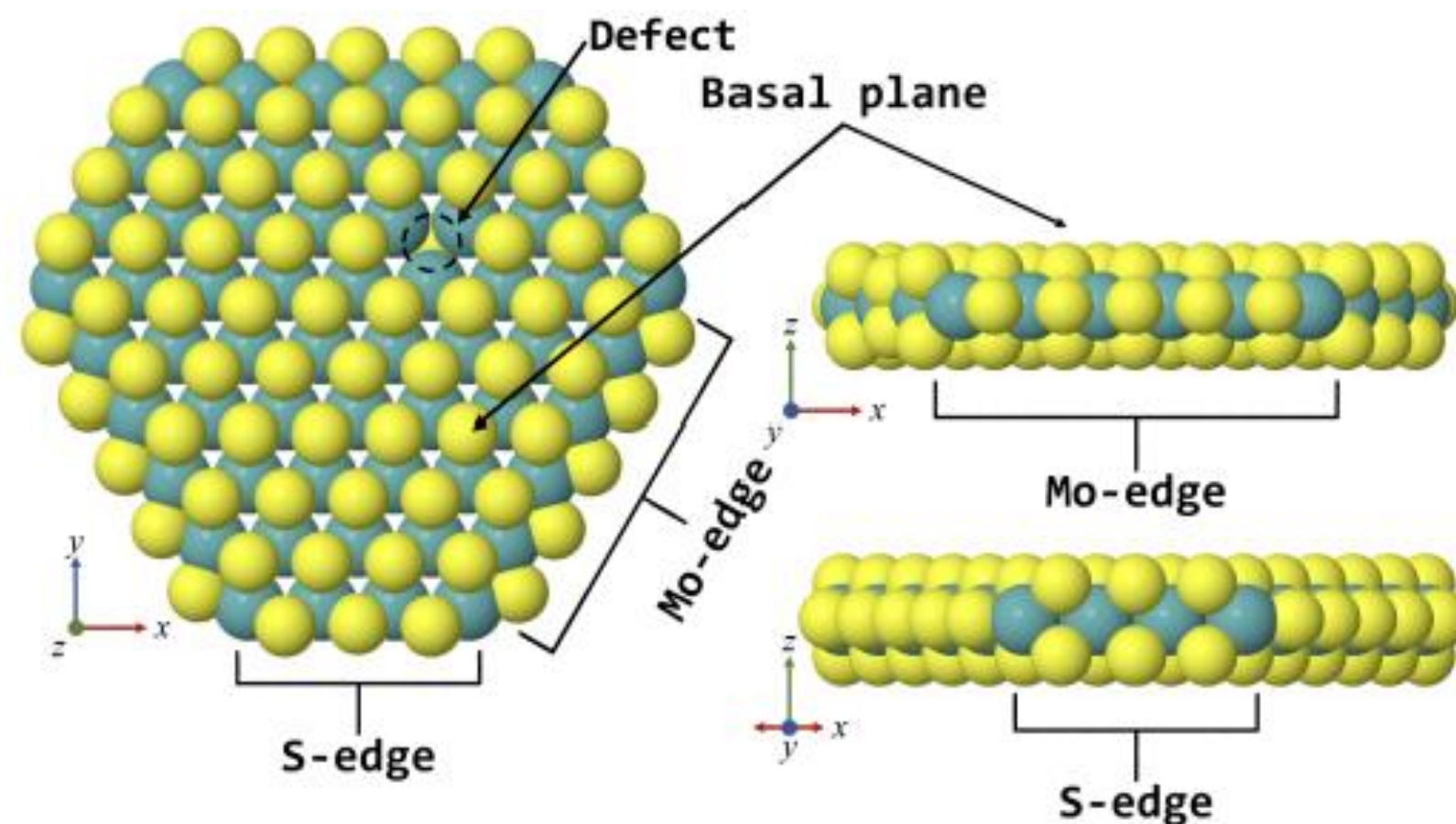
Kayla Prendergast, Christopher S. Mills, Anna L. Garden
Department of Chemistry, University of Otago

Email:
preka411@student.otago.ac.nz

MoS₂ as an HER catalyst

MoS₂ is a promising candidate for HER catalysis as it is earth abundant, inexpensive and highly tuneable.

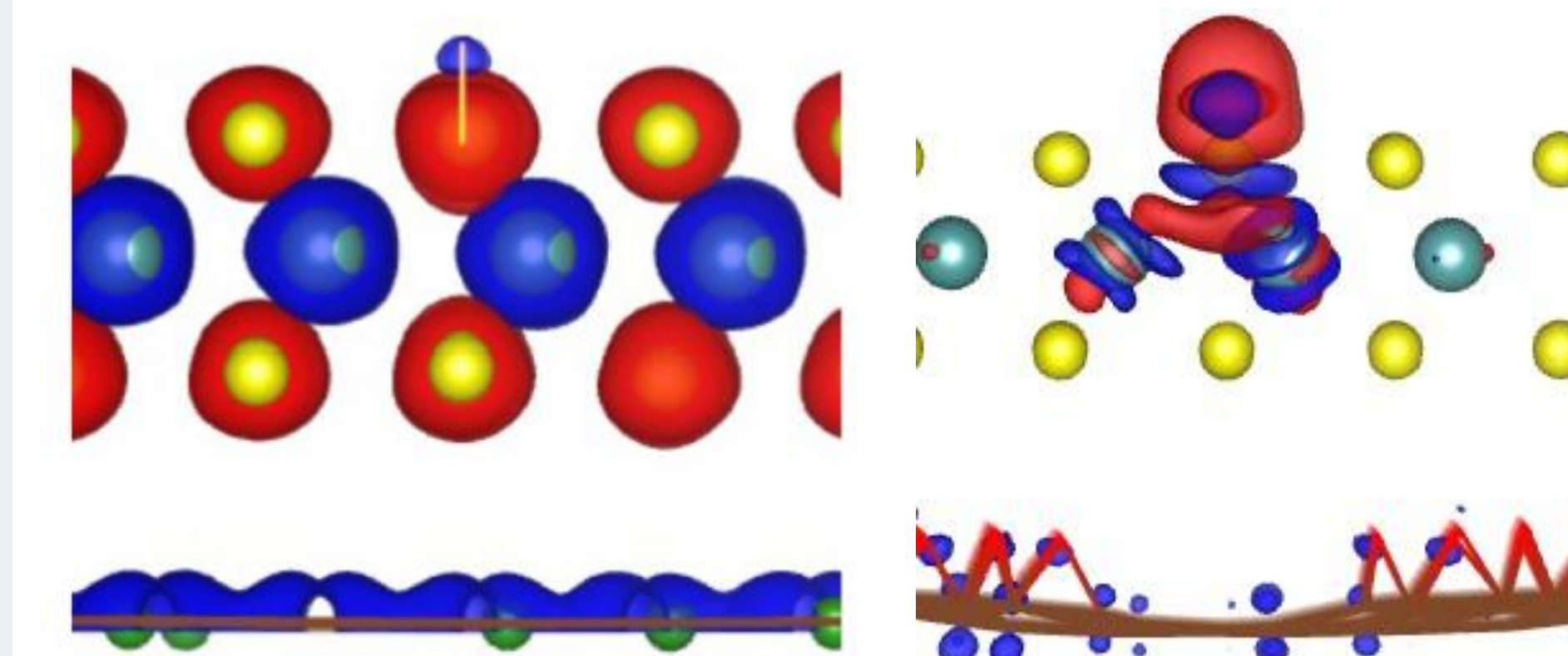
- Active sites competitive with platinum-based catalysts
- Edge and defect sites are activated towards the HER, achieving Gibbs free energy values of up to ± 0.08 eV.¹
- The pristine basal plane is considered inactive towards the HER, but can be tuned using supports and twistrionics



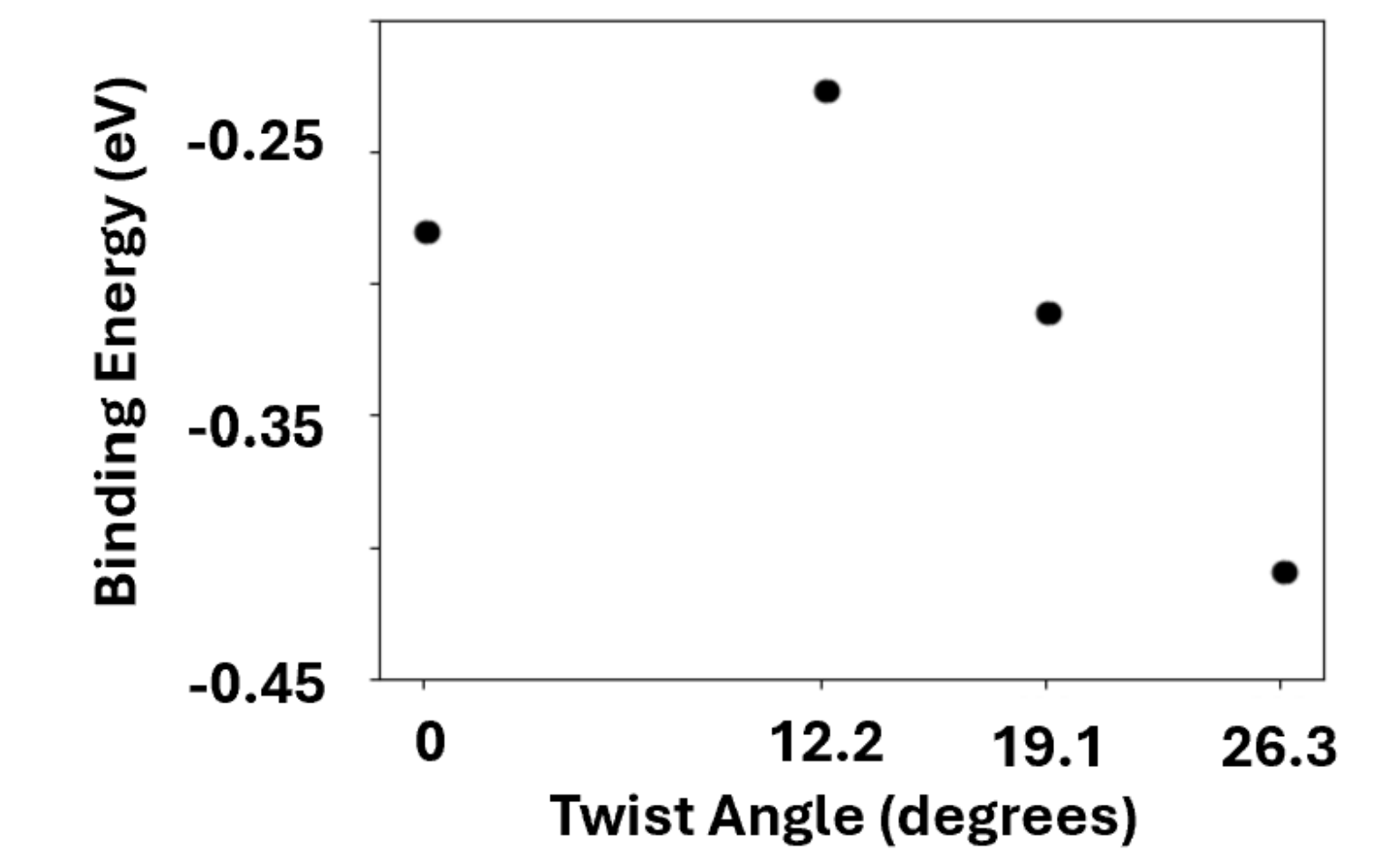
- Gibbs energy ($\Delta G_{H_{ads}}$) used as descriptor of the hydrogen evolution reaction (HER)
- Defect sites and relative twist angles can bring $\Delta G_{H_{ads}}$ closer to the optimal 0 eV

Twisted MoS₂ systems

- Conductive supports, BDG and GO-epoxide, accumulate electron density upon H adsorption
- Involved in binding mechanism since accommodate charge that would otherwise remain at the surface
- Hypothesized that this charge movement to the support makes these systems more susceptible to applied twist angles



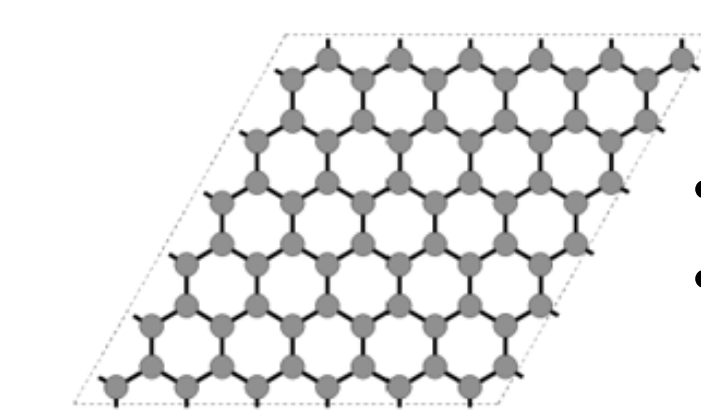
Charge density difference plots of BDG (left) and GO-epoxide (right), after H adsorption. Blue is negative charge accumulation, red is negative charge depletion.



- BDG support showed significant alteration of binding energy when twist angles applied
- Position of H adsorbate kept consistent
- No correlation between binding energy and relevant changes in electronic structure for the pristine or defect systems
- Electronic structure analysed via density of states (DOS), with specific valence band maximum values as key metrics

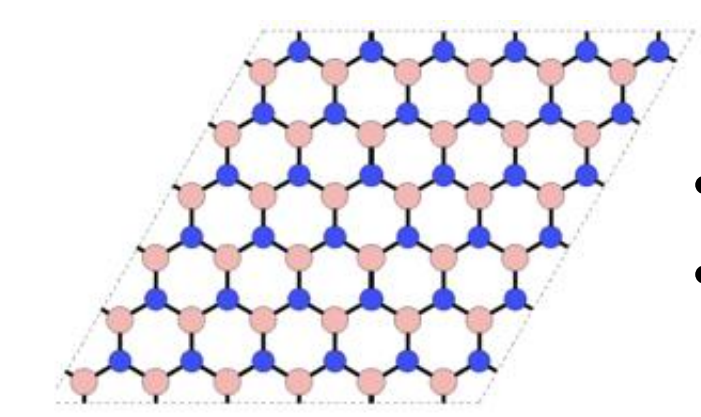
Supported MoS₂ systems

Insulating, semiconductive and conductive supporting materials selected from prior work by Ruffman *et al.* based on their performance tuning pristine MoS₂.²



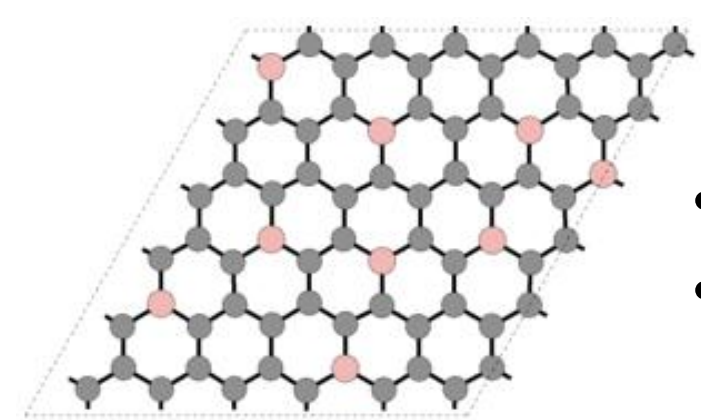
Graphene

- Semiconductive, unlikely to be involved in H adsorption
- Defect binding energies vary between -0.27 and 1.50 eV across H adsorption sites



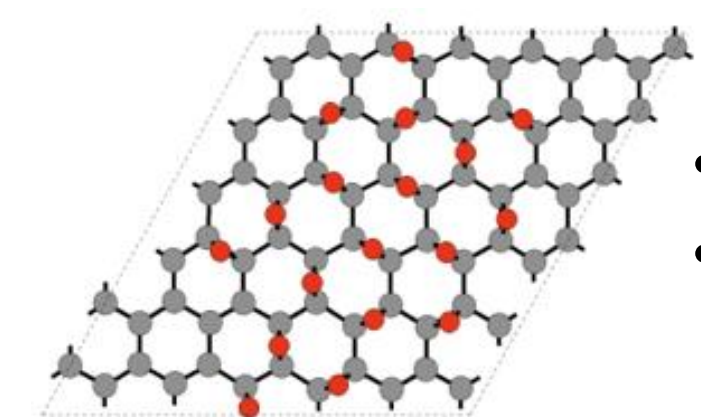
Hexagonal boron nitride (HBN)

- Insulating, not involved in H adsorption
- Defect binding energies vary between -0.28 and 1.27 eV across H adsorption sites



Boron-doped graphene (BDG, 12%)

- Conductive, becomes involved in H adsorption
- Defect binding energies vary between -0.40 and 1.32 eV across H adsorption sites

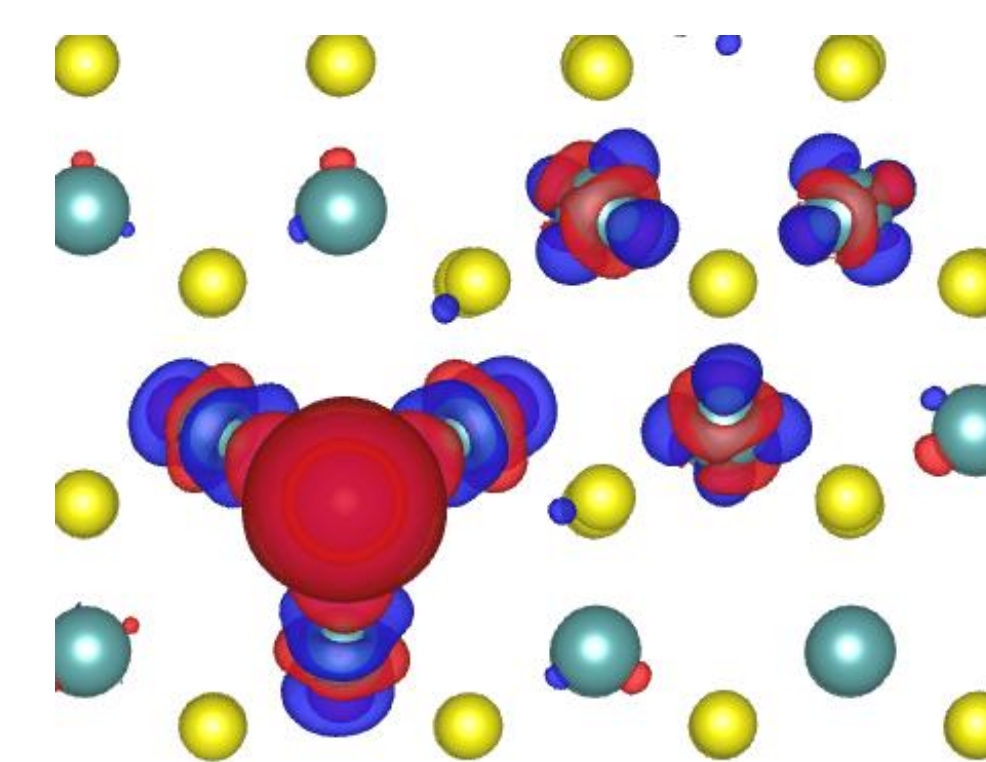


Graphene-oxide epoxide (25%)

- Conductive, becomes involved in H adsorption
- Defect binding energies vary between -0.42 and 1.52 eV across H adsorption sites

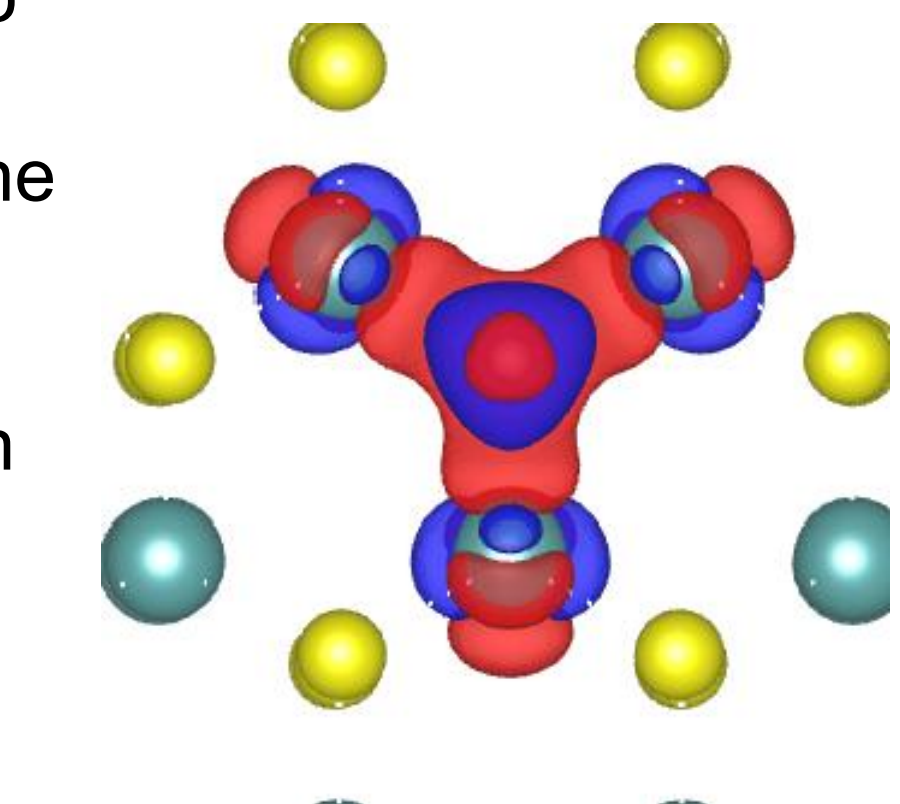
H adsorption on defected MoS₂

- The defect tunes surrounding atoms
- When S-H bond forms near the S defect, electron density (blue) moves from S to neighbouring Mo atoms, and the Mo atoms of the defect position
- Charge displacement beyond the nearest Mo atoms is absent for pristine MoS₂



Charge density difference plots, after H adsorption. Blue is negative charge accumulation, red is negative charge depletion.

- When H adsorbs in the vacancy, no S-H bond forms
- Instead, electron density shifts to the three nearest Mo atoms
- Proposed binding mechanism is similar to H adsorption on transition metal surfaces
- Binding energy in the vacancy is significantly stronger than nearby positions, by up to 1.50 eV



Computational methods

- DFT calculations performed with the Vienna *Ab Initio* Simulation Package (VASP, version 5.4.4)
- PBE+DFT-D3 functional used throughout this work.³
- MoS₂ modelled with supports and twisted



Future directions

- Additional conductive supports and twist angles will be investigated
- BDG support was buckled at some twist angles. More exploration will establish whether this affects the binding mechanism and/or electronics
- Binding energies will be converted to Gibbs free energy values, to more easily compare to the literature

References:
1. Tsai, C.; Li, H.; Park, S.; Han, H.; Norskov, J. K.; Zheng, X.; Abild-Pedersen F. *Nat. Commun.* **2017**, *8*, 15113.

2. Ruffman, C.; Gordon, C. K.; Gilmour, J. T. A.; Mackenzie, F. D.; Garden, A. L. *Nanoscale* **2021**, *13*, 3106-3118.
3. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, S. *J. Chem. Phys.* **2010**, *132*, 154104.