

Electronic structure of defect-modulated MoS₂: HER catalytic activity

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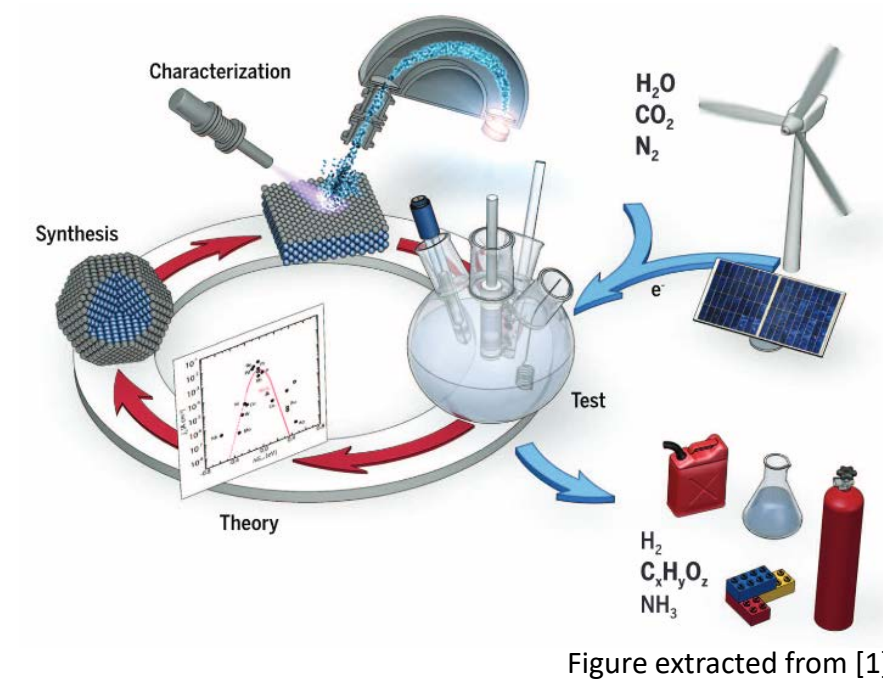
Motivation

MoS₂, an abundant and inexpensive mineral, is seen as a promising material for the future of renewable energy. An efficient Hydrogen Evolution Reaction (HER), i.e., hydrogen production through water electrolysis, demands replacing platinum group metals catalyst altogether [1]. However, pristine MoS₂ is not very efficient as catalysts. Defect engineering is essential to achieve operational platinum-like performance.

Goal

Our work aims to boost the HER performance of MoS₂ by increasing the overall number of catalytically active sites. To this end, we will take advantage of the preferential sublimation and sputtering of S.

Sustainable electrochemical energy conversion



Water, carbon dioxide, and nitrogen can electrochemically be converted into value-added products (e.g., hydrogen, hydrocarbons, oxygenates, and ammonia) using renewable energy.

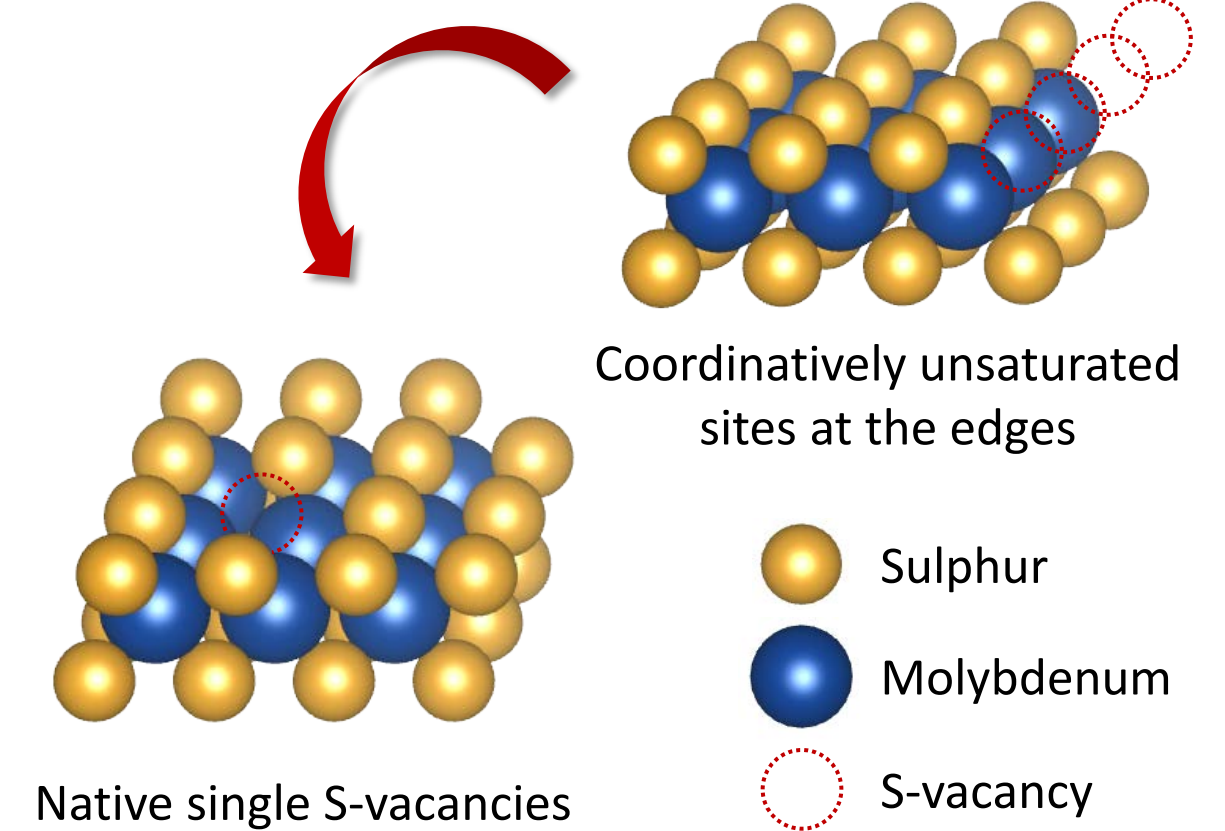
Catalytic active sites for HER

Active catalysts are required to minimize the overpotential necessary to drive the water splitting. This reaction can be synthesized in a two-step model:

- (1) Reactant binding
Volmer step: $\text{H}^+ + \text{e}^- + * \rightarrow \text{H}^*$
- (2) Product release
Heyrovsky step: $\text{H}^* + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2 + *$
Tafel step: $2\text{H}^* \rightarrow \text{H}_2 + 2*$

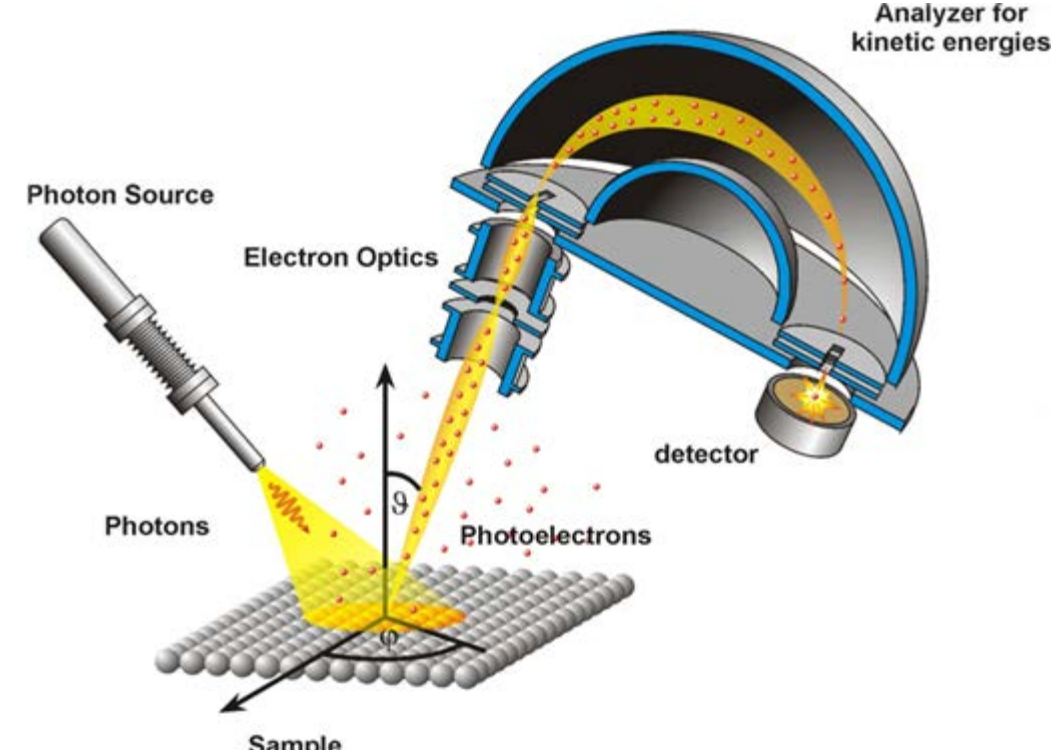
Since the MoS₂(0001) basal plane intrinsically lacks exposed Mo atoms, much effort has been devoted to increasing the density of these defects [2].

The total reaction rate is primarily determined by hydrogen bonding to the catalyst. In MoS₂, the catalytically active sites for bonding are the exposed Mo atoms found at the edges and near S-vacancies.



Experimental

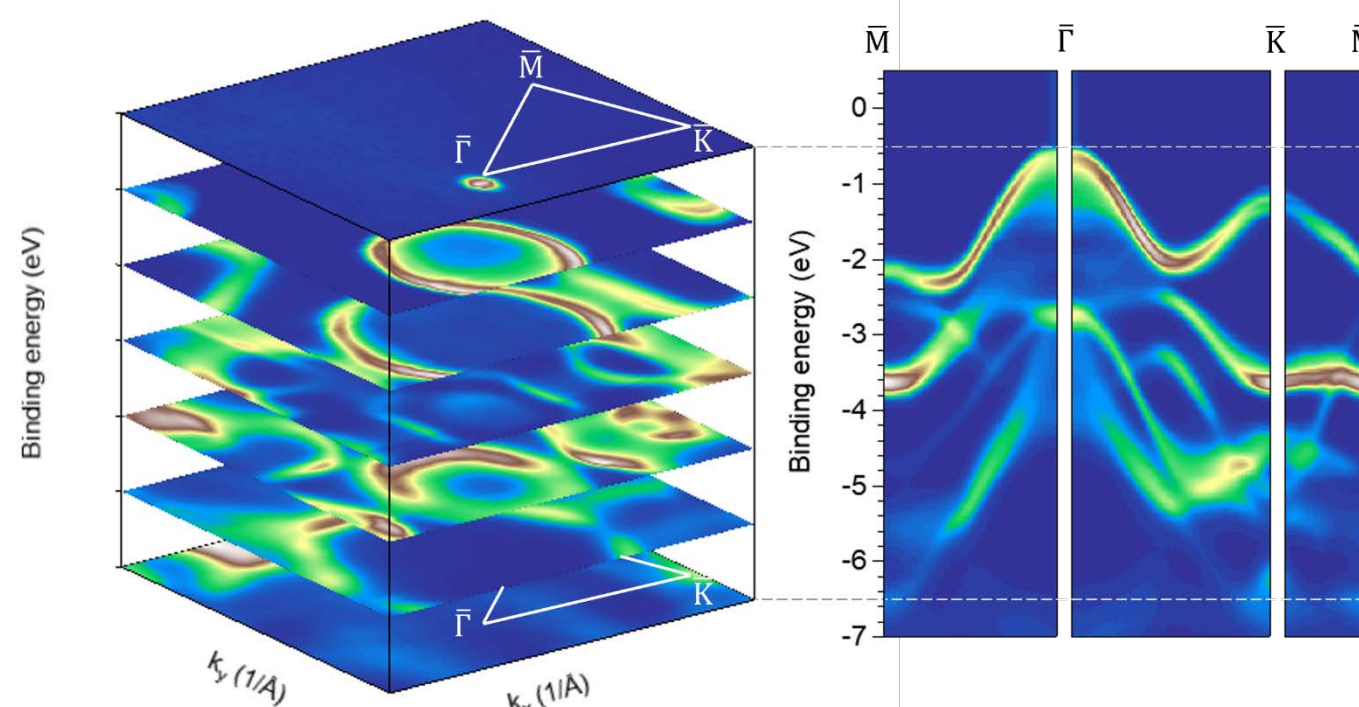
Angle-Resolved Photoemission Spectroscopy (ARPES)



ARPES measures the complete set of quantum numbers of the electron. The measured energy, momentum and spin of the photoelectrons are linked to the binding energy, quasimomentum, and spin that the electron had in the solid.

- Energy range: 10 - 100 eV
- Energy resolution 1.8 meV
- Available light polarizations: LV, LH, CP_±
- Sample temperature: 4 – 500 K

MoS₂:Nb band structure



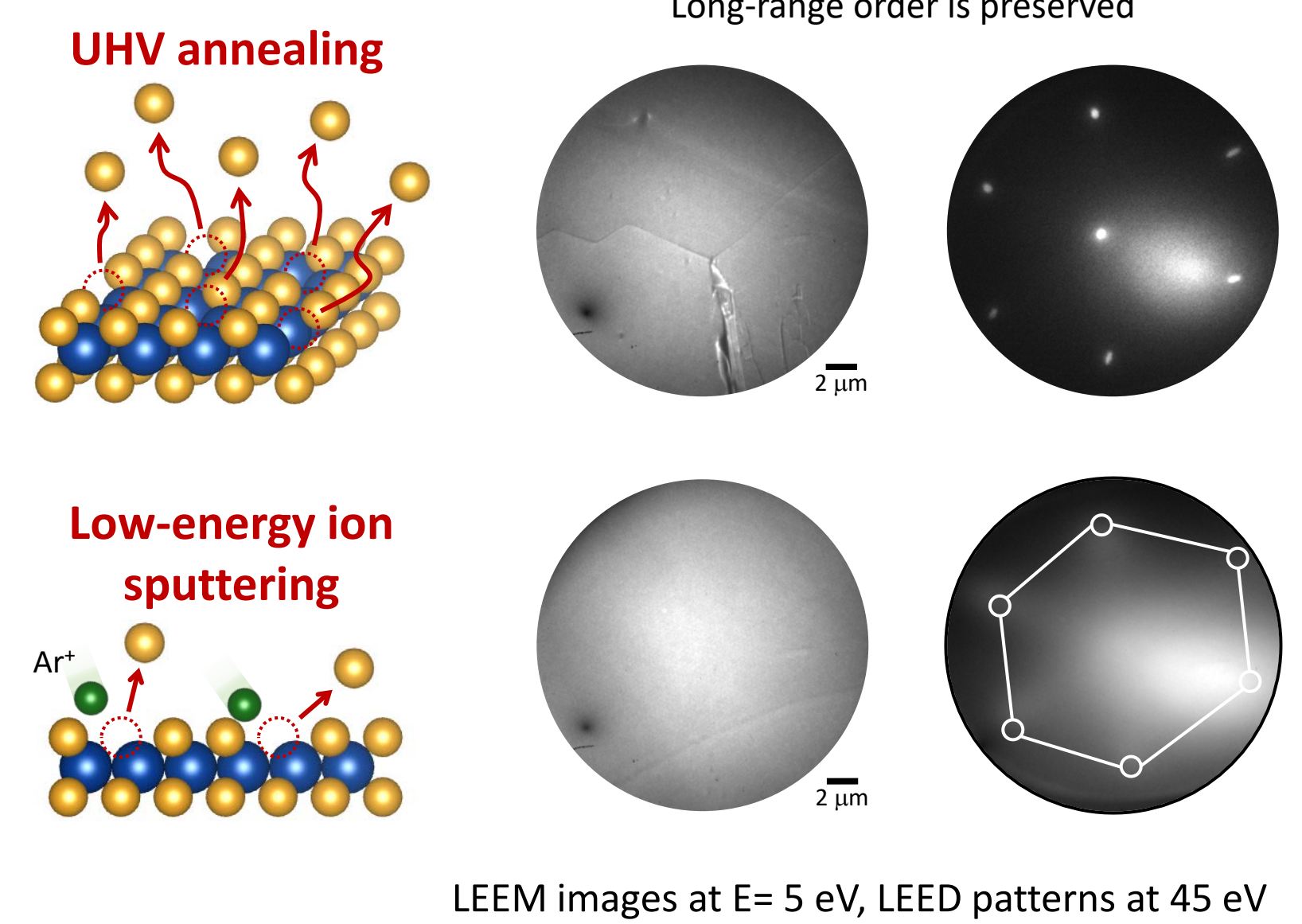
Structural modification

Defect engineering by two alternative methods

Tailoring the electronic properties of MoS₂ is possible since they are extremely defect-dependent.

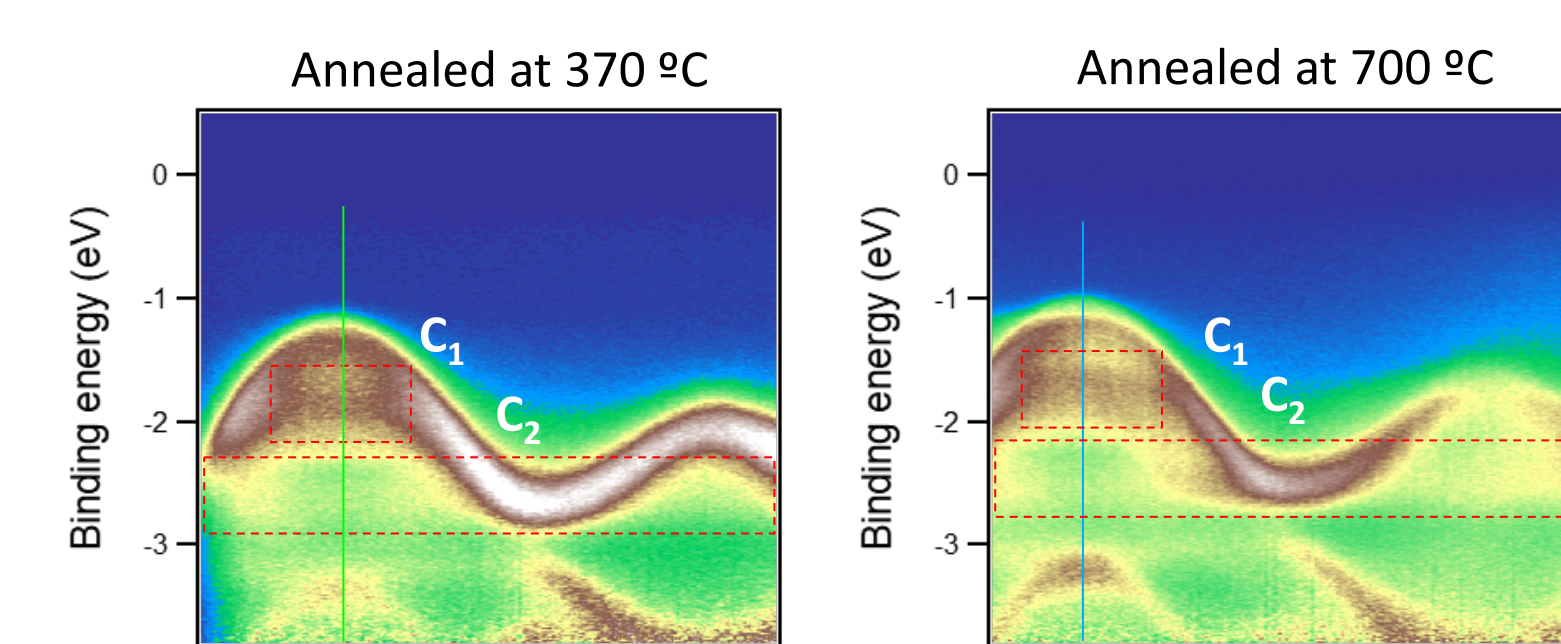
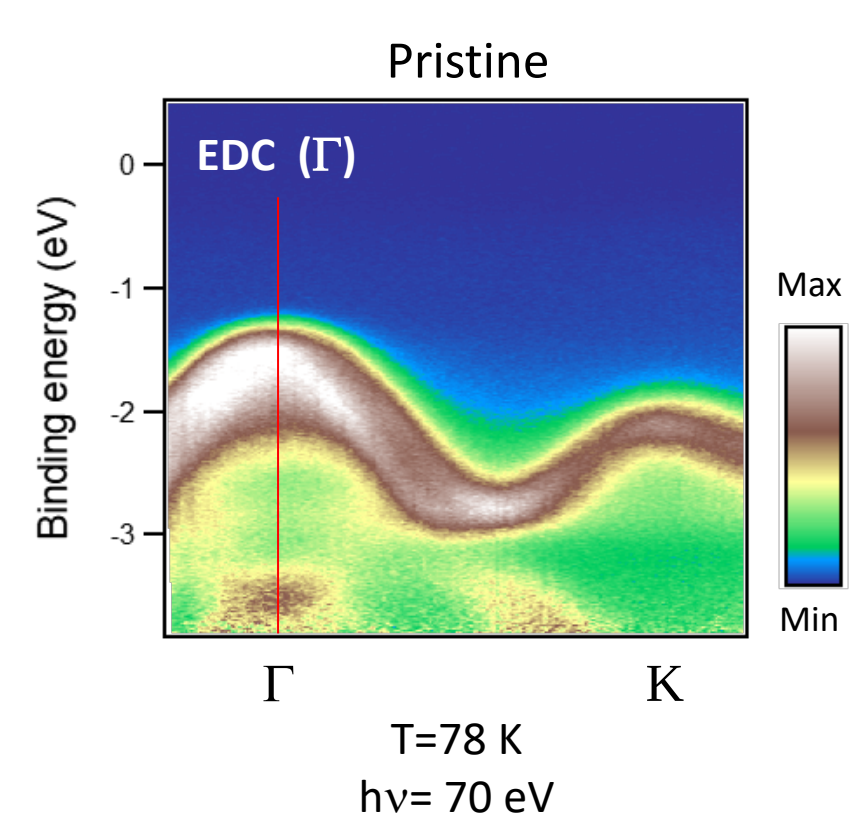
We can induce defects in the structure, by two methods:

- (1) UHV annealing induces desorption of S atoms, leaving behind (mostly) single and double vacancies [3].
- (2) Low-energy ion sputtering is an efficient tool for creating single S-vacancies since the displacement threshold energy of S is six times lower than that of Mo [4].

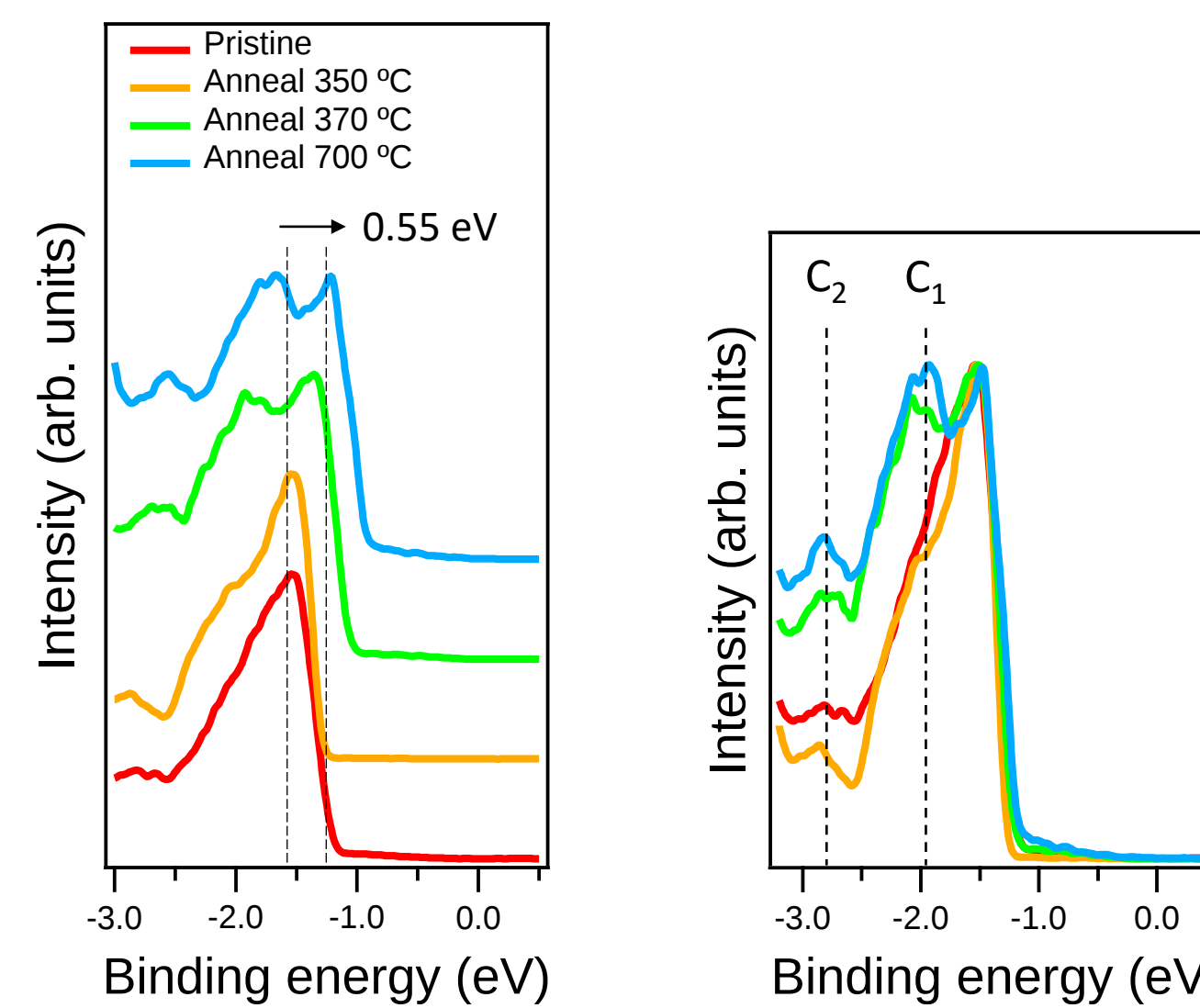


Results

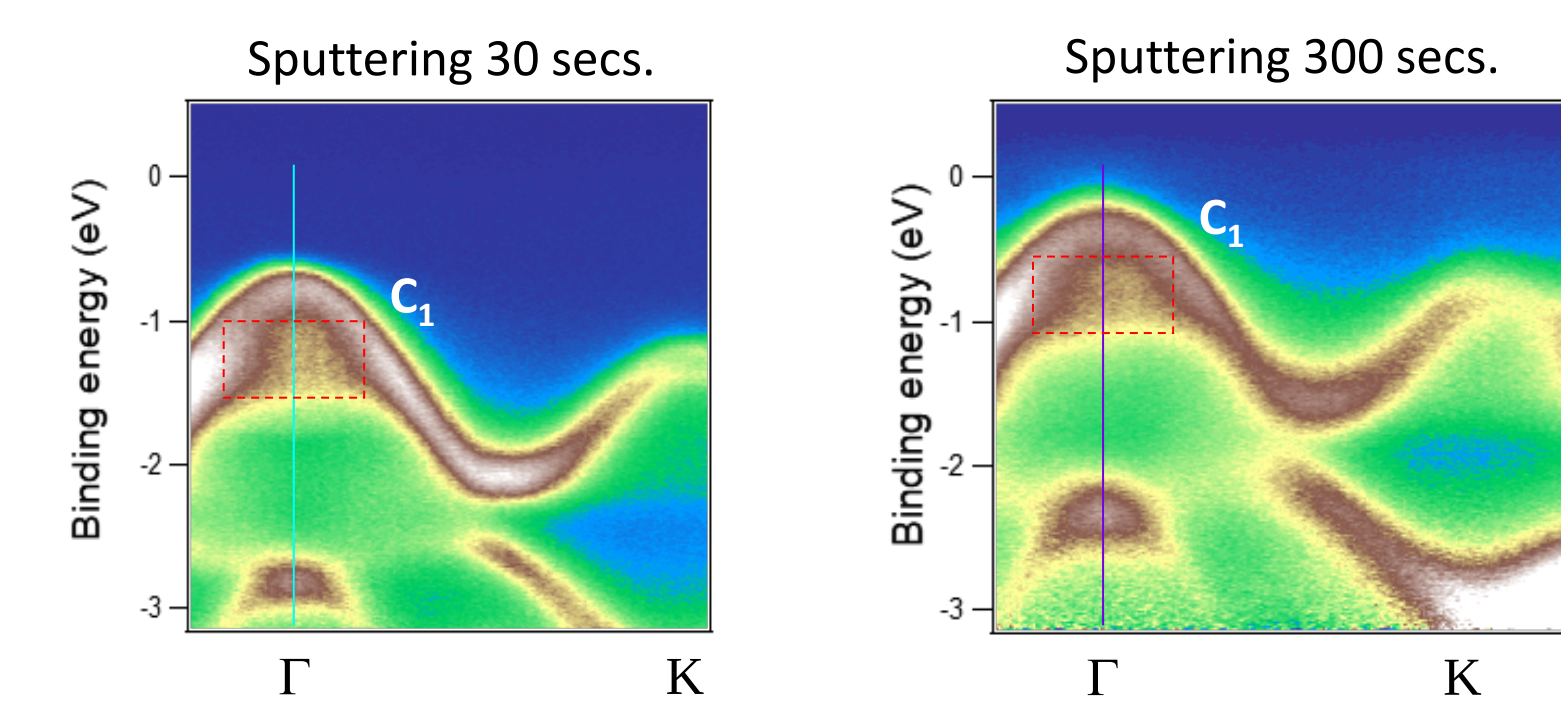
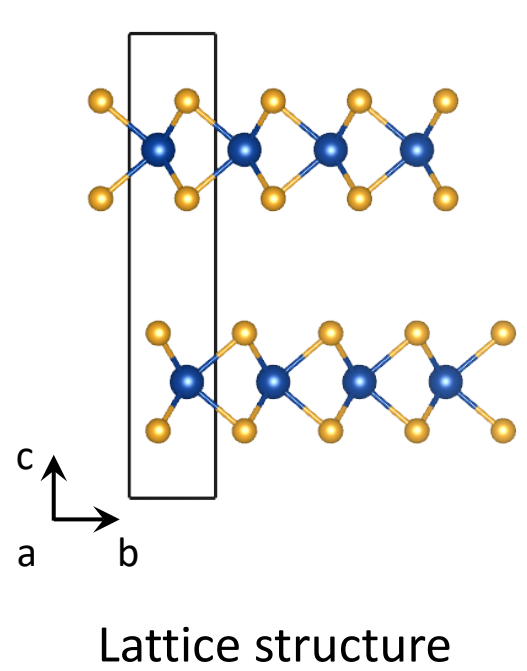
Annealing at UHV



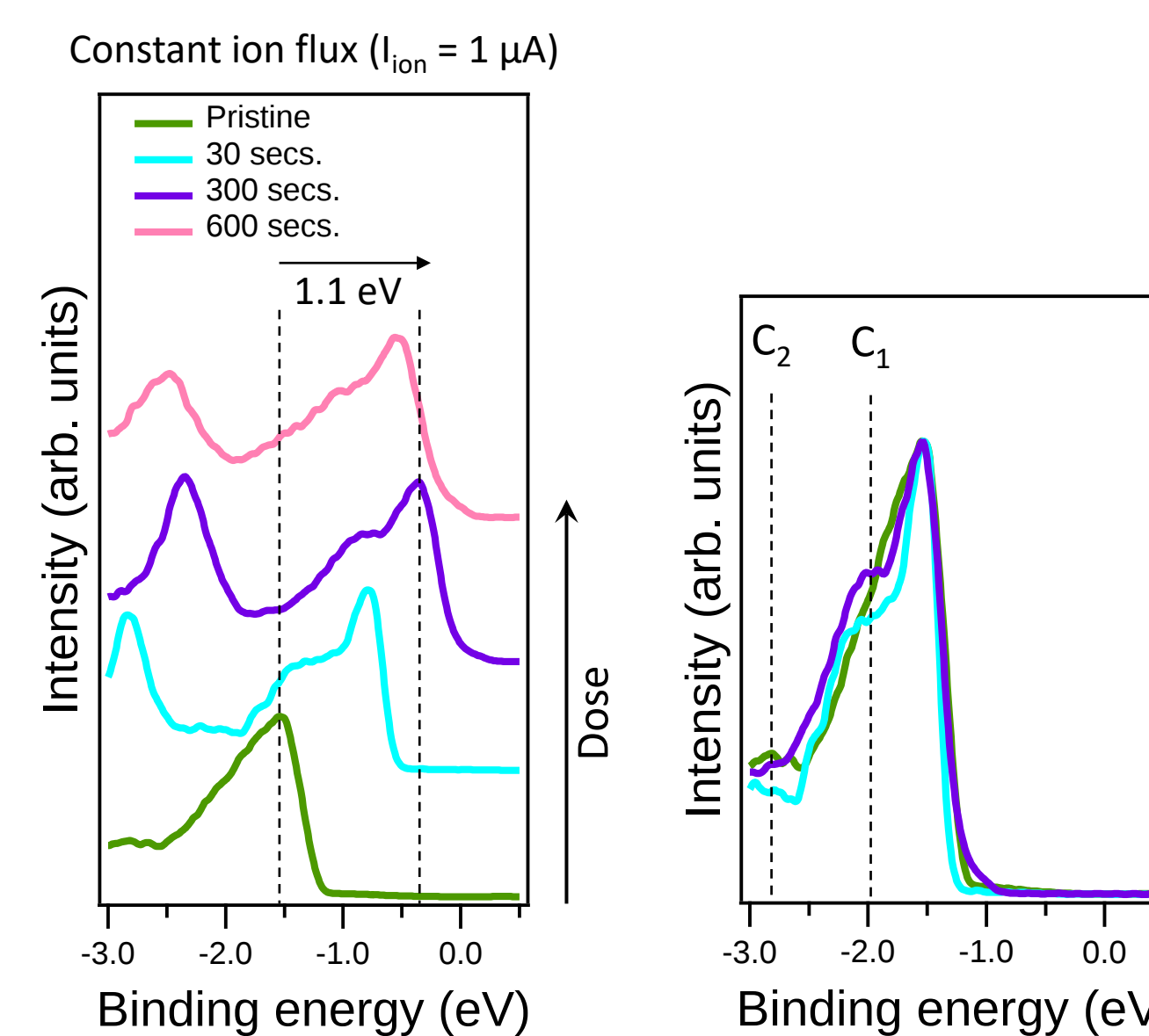
- We observe a rigid band shifting towards lower BE (p-type shift), consistent with a redistribution of charge from vacancies to neighbouring atoms.
- The gradual increase of the C₁ and C₂ peaks with temperature shows the development of two sulphur defect-related bands [5].



Low-energy ion sputtering



- Argon sputtering yields larger shifting's, eventually metallizing the bands (the valence band maximum (VBM) crosses the Fermi level).
- In contrast to the annealing method, the peaks C₁ and C₂ hardly grow at all. The defect bands are not visible.
- The p-shifting trend turnovers at larger doses (600 secs.).

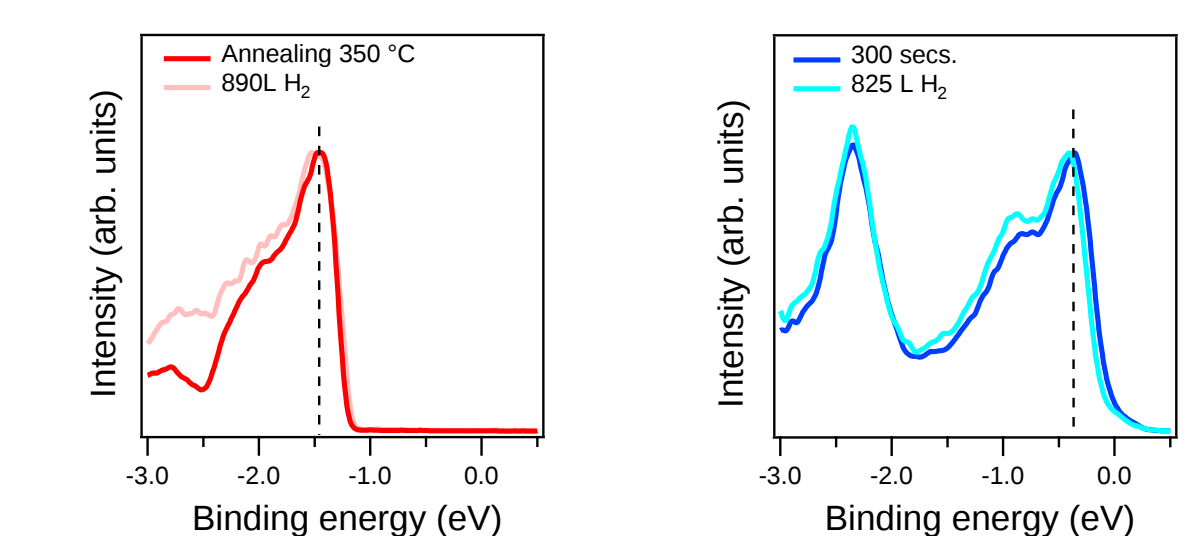


Boosting the HER activity on MoS₂

Inert surface

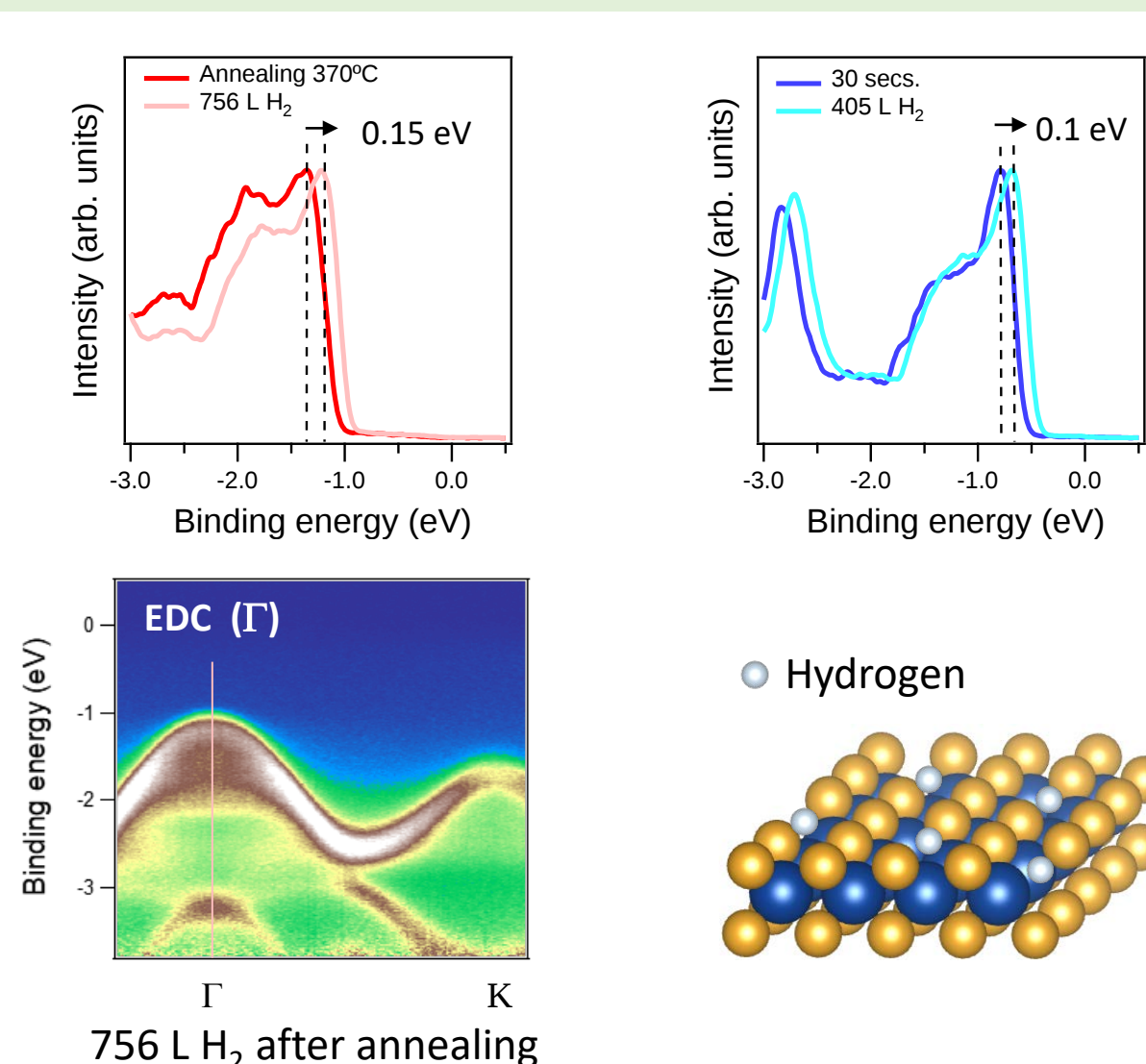
No shifting is observed after significative H₂ dosing.

- Annealing at 350 °C produces low number of defects. There are no sites available for H₂ binding.
- Large sputtering doses produce a metallic surface inert to H₂ binding.



Active surface

The defects created are catalytically active. Hydrogen binds to the defects, so the VBM is displaced (defect passivation)



Conclusions

- Different defective surfaces have been created by two different methods: annealing at UHV and low-energy ion sputtering. Each method generates different types of defects.
- Annealing at UHV generates defect bands within the valence band. These bands have been predicted theoretically but had not been experimentally observed until this work.
- Low-energy ion sputtering is an effective method for removing S and generating defects.
- We can create catalytically active hydrogen-sensitive surfaces. VBM shift and band narrowing confirms that hydrogen surface bonding is taking place.
- Large sputtering doses generates an inert metallic surface. This confirms that only exposed Mo atoms surrounded by a sulphur environment (as in S-vacancies) are the catalytically active.

References

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Acknowledgements

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