Constructing Tunable Electrides on Monolayer TMDCs

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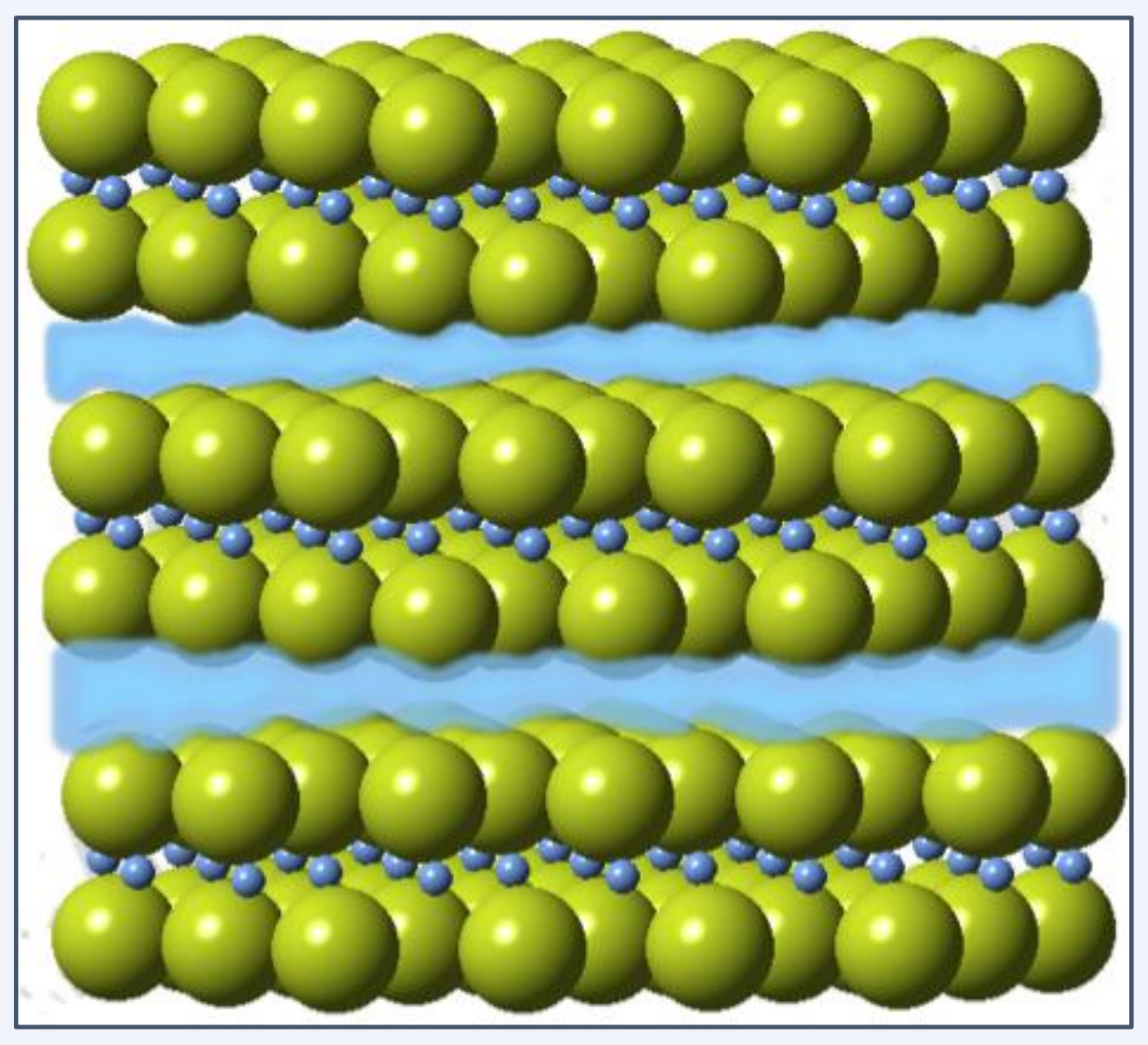
Abstract

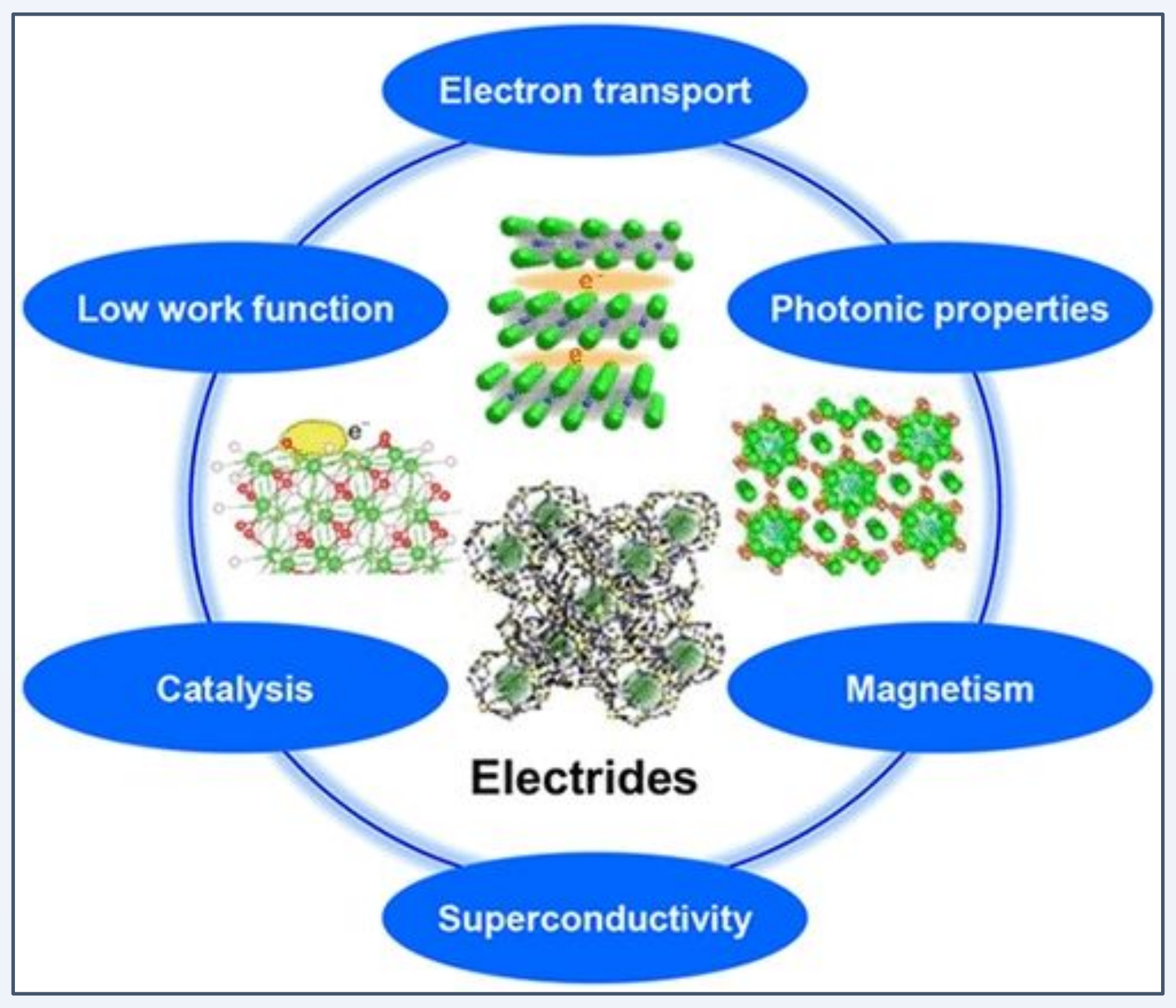
Electrides have emerged as promising materials with exotic properties due to the presence of localized electrons detached from all atoms. Despite the continuous discovery of many new electrides, most of them are based on atypical compositions, and their applications require an inert surface structure to passivate reactive excess electrons.Here, we demonstrate a different route to attain tunable electrides. We first report that monolayer transition metal dichalcogenides (TMDCs) exhibit weak electride characteristics, which is the remainder of the electride feature of the transition metal sublattice. By Introducing chalcogen vacancies, the enhanced electride characteristics are comparable to those of known electrides. Since the precise tailoring of the chalcogen vacancy concentration has been achieved experimentally, we proposed that TMDCs can be used to build electrides with controllable intensities. Furthermore, we demonstrate that theelectride states at the chalcogen vacancy of monolayer TMDCs will play an important role in catalyzing hydrogen evolution reactions.

Electride Chemistry

- Electrides are materials where electrons are confined in interstitial voids, effectively acting as anions.
- They exhibit high electron mobility and low work functions, which are beneficial for catalytic and electronic applications.
- Their ability to donate electrons provide the potential for applications in next-generation electronic components that use less energy and operate faster
- Unique and electron-rich environments can aid in reactions necessary to store and convert energy, resulting in improved sustainability



Electride Ca_2N with electrons confined between layers



Electron transport

Low work function

Photonic properties

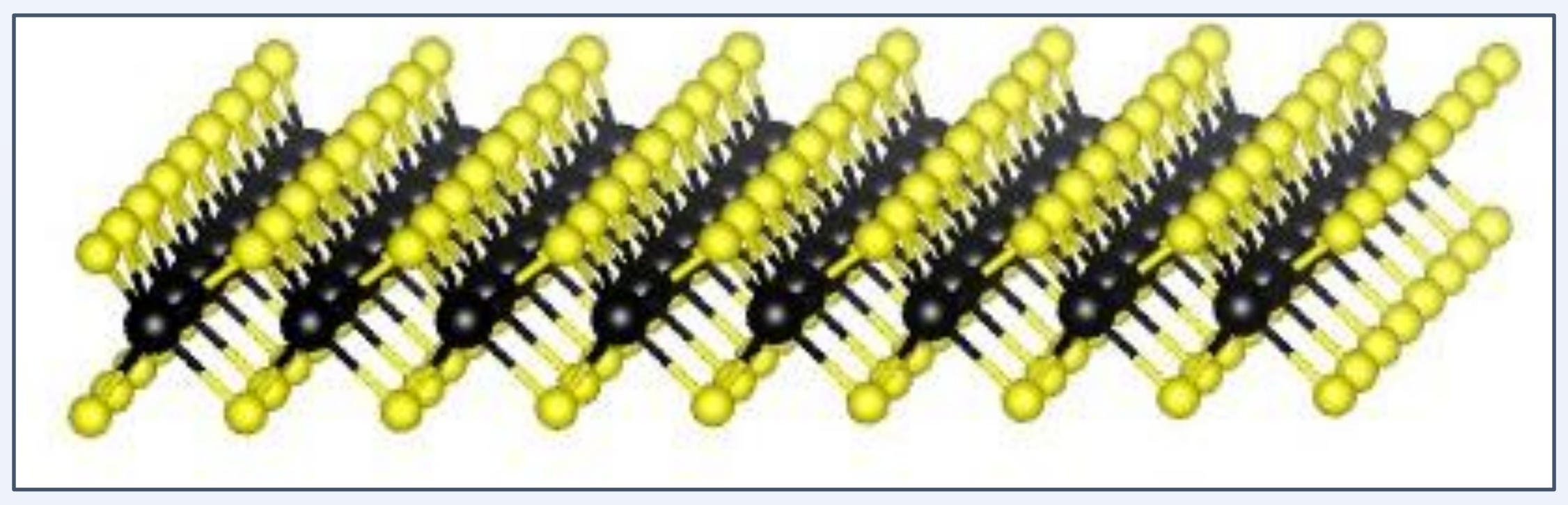
Catalysis

Magnetism

Electrides

Superconductivity

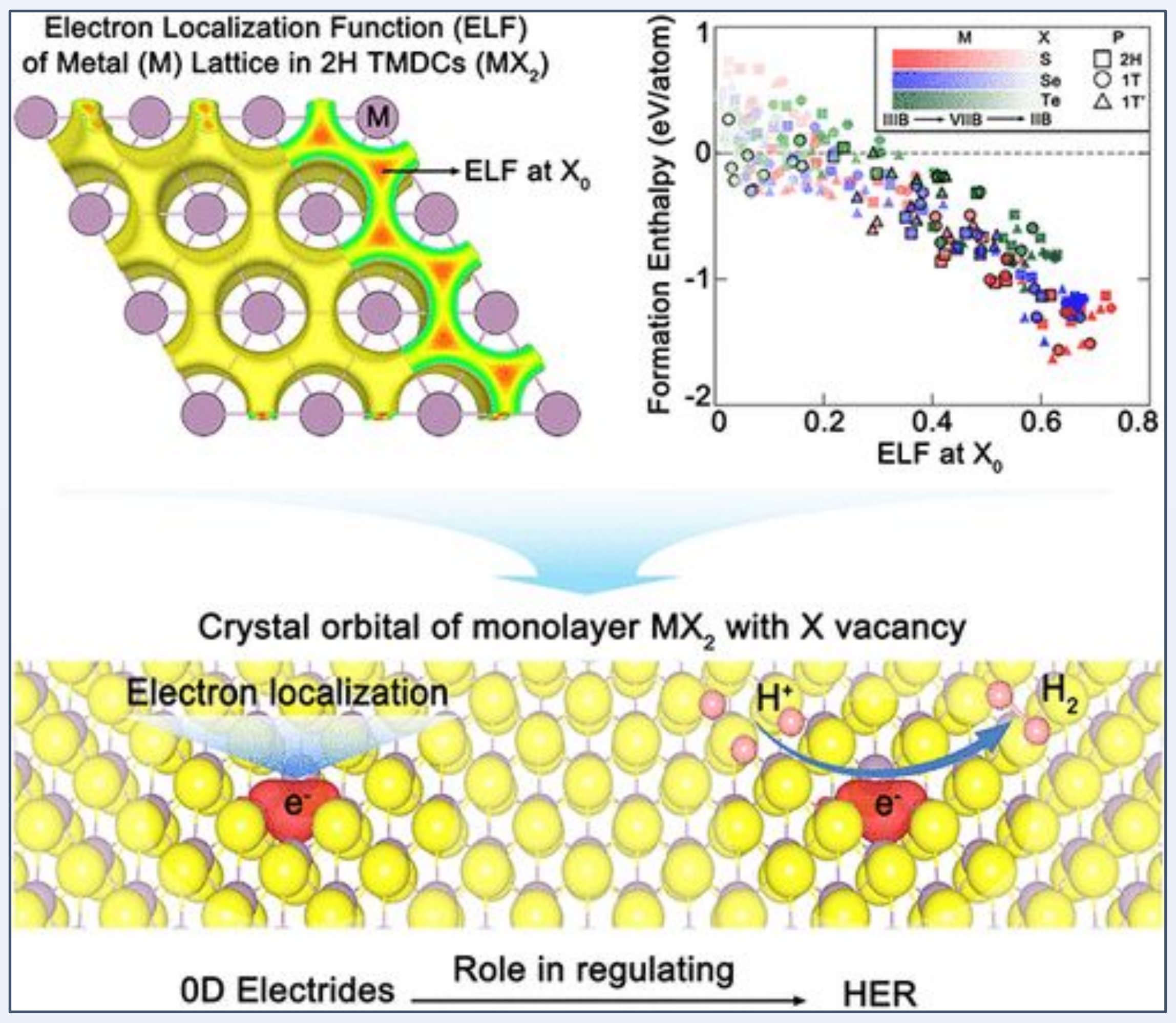
Transition Metal Dichalcogenides (TMDCs)



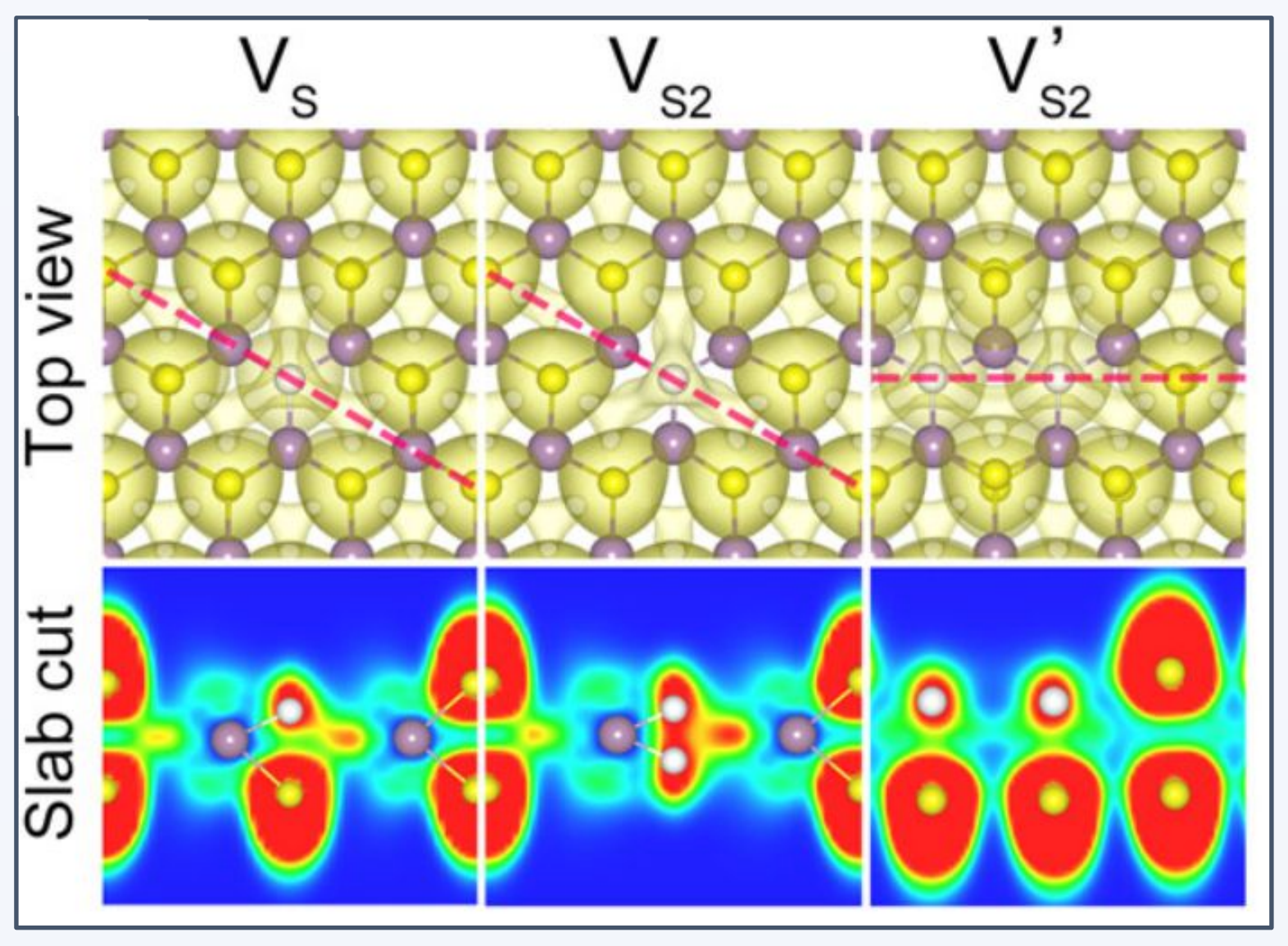
Typical TMDC Structure

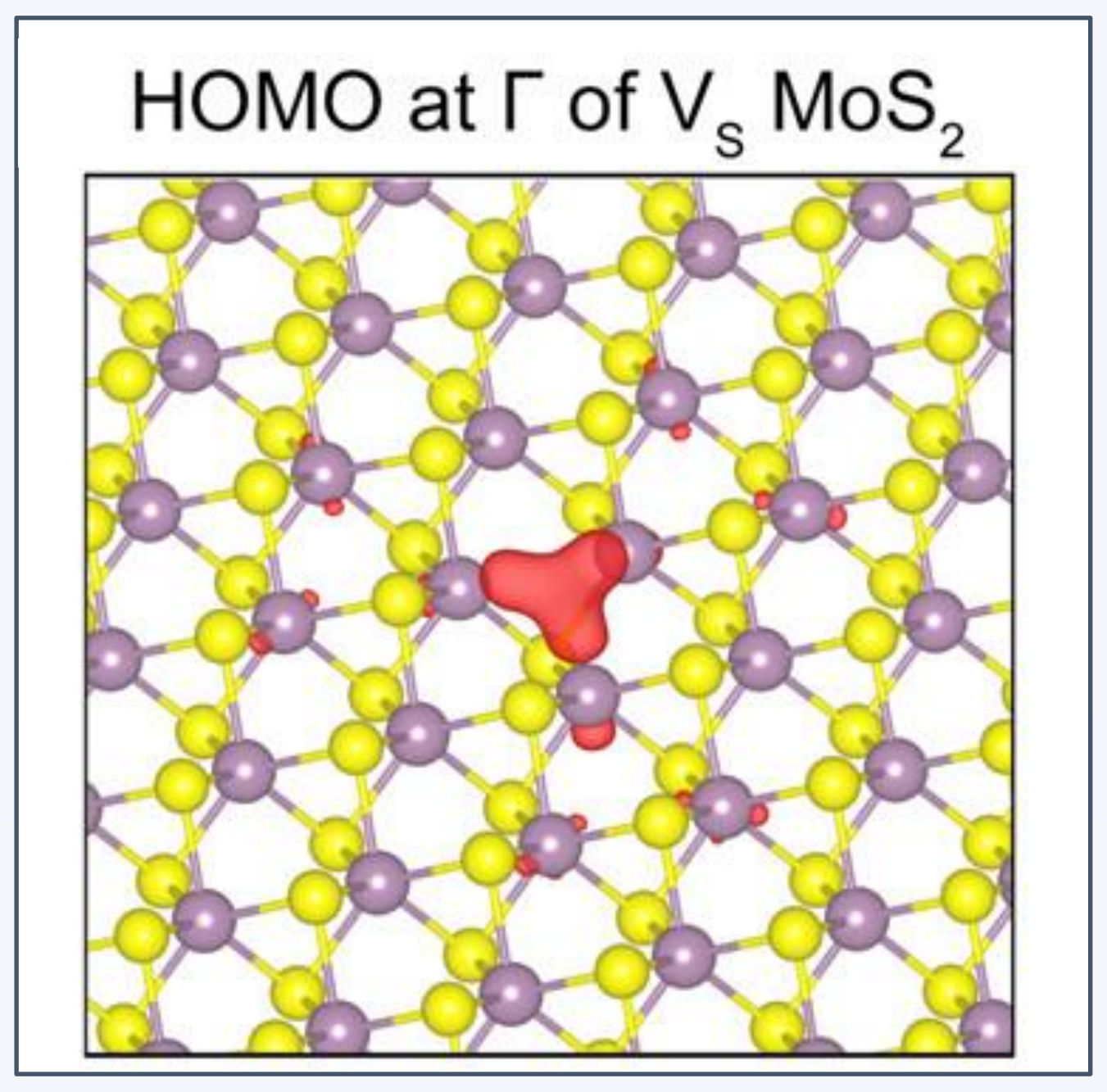
- TMDCs have the general formula MX_2, where M is a transition metal (e.g., Mo, W) and X is a chalcogen (e.g., S, Se, Te)

- These materials are easily exfoliated into monolayers, providing a versatile platform for 2D material research.
- TMDCs exhibit tunable band gaps and high mechanical flexibility, making them ideal for nanoelectronics and optoelectronics.
- They are extensively studied for catalytic applications, particularly in the hydrogen evolution reaction (HER), due to their surface-active sites.

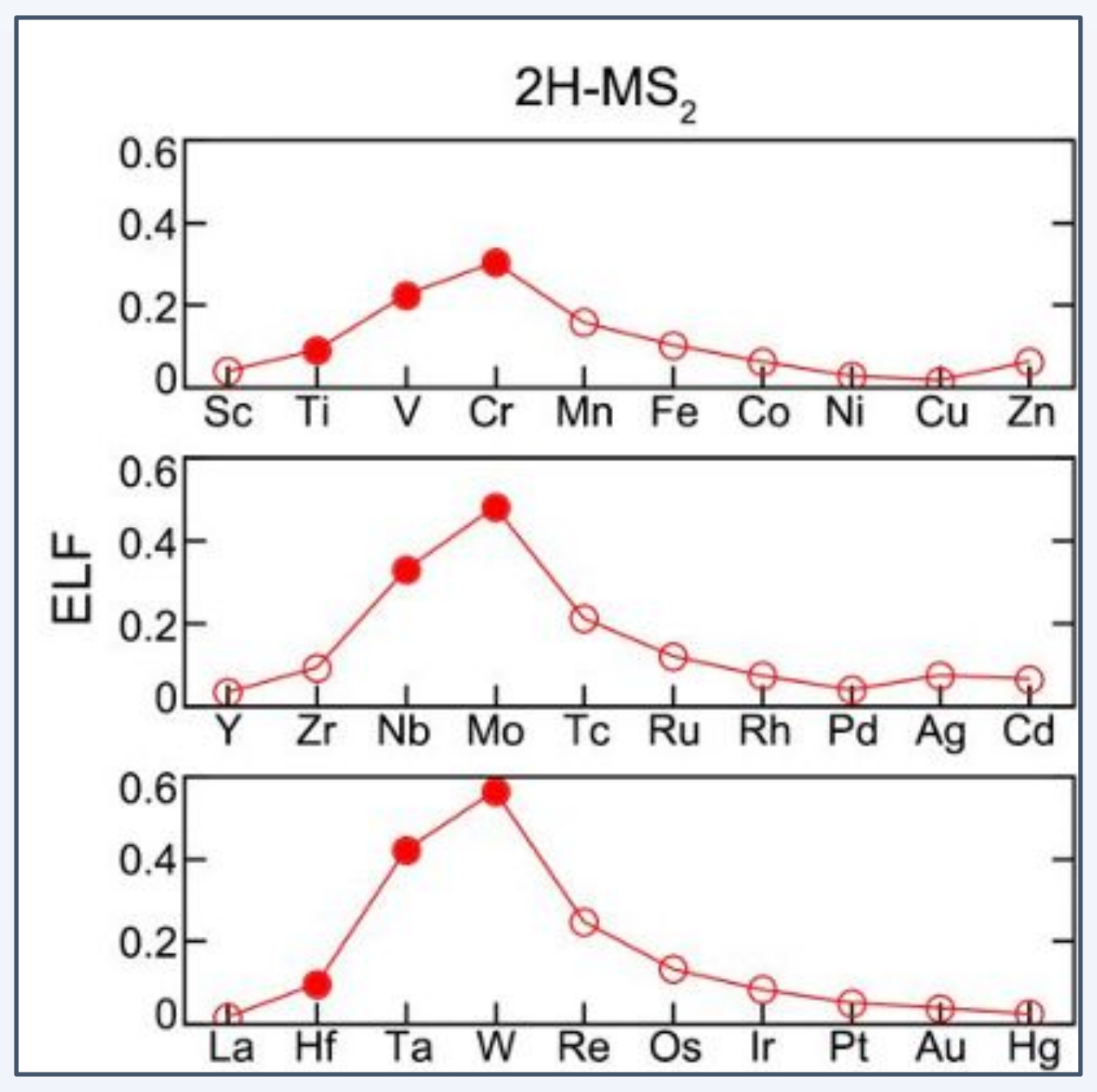


Tunable Electrides

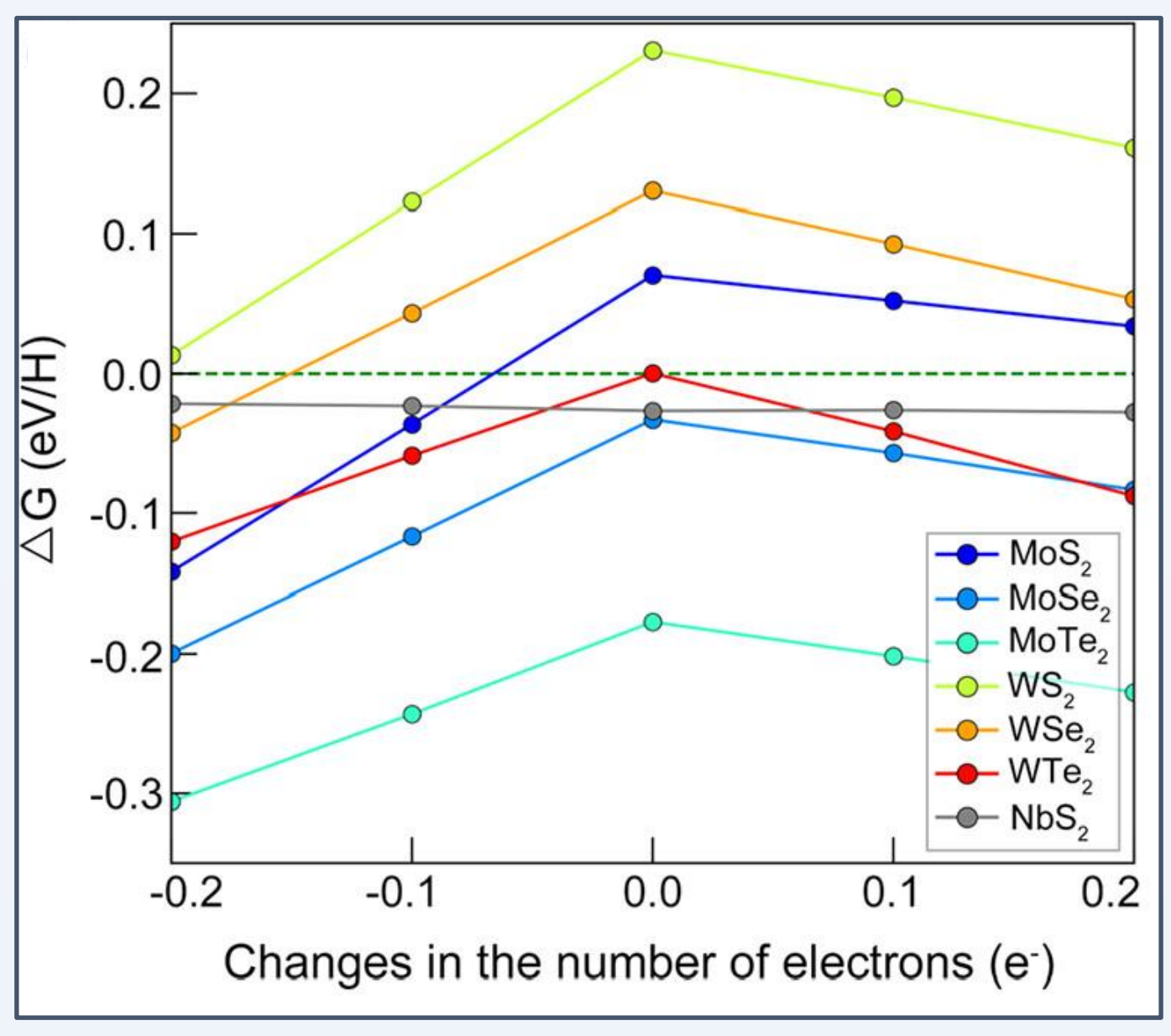




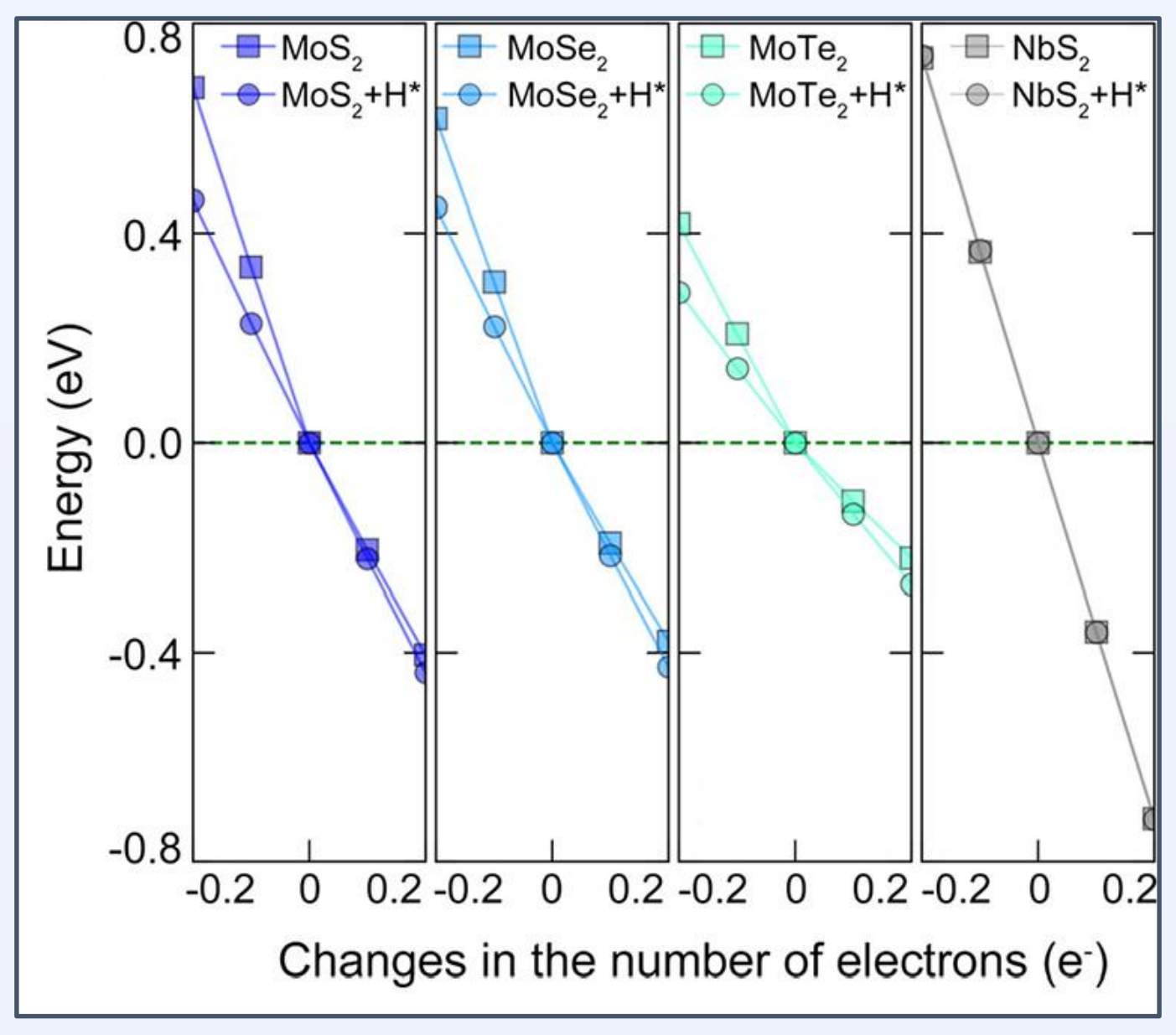
- ELF plots display pronounced electron localization at vacancy sites, highlighting the tunability of the electride based on vacancy type and location within the lattice
- The partial charge densities of the highest occupied molecular orbital shows electride nature of MoS_2 is determined by localized electrons in the vacancy
- Comparative studies across different TMDC systems (e.g., MoS_2 versus WS_2) underscore the critical role of metal identity in dictating electride strength and catalytic performance.

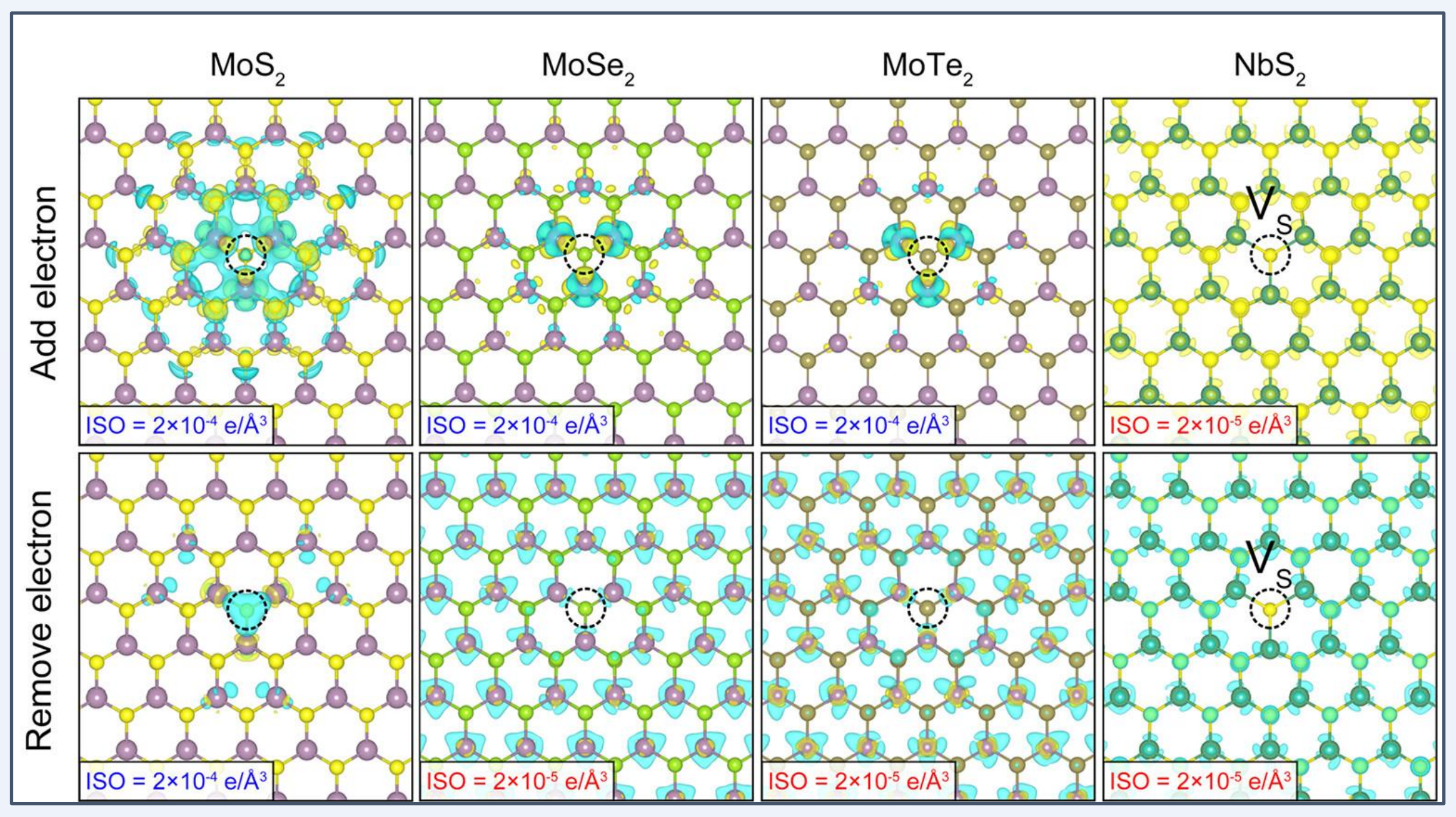


Vacancy-Enhanced HER Catalysis



- Small changes in number of electrons significantly affects hydrogen adsorption free energy, calculated by: $\Delta G(H^*)=\Delta E(H^*)+\Delta E_{ZPE}-T\Delta S$
- Simulated electron doping demonstrates that adjusting the electron occupancy further optimizes the catalytic performance, ensuring dynamic control over HER activity.
- Charge density difference plots confirm that electron donation or removal concentrates around the defect sites, showing a clear link between the vacancy engineering, local electronic structure, and catalytic behavior





Conclusions

- Introducing controlled chalcogen vacancies in monolayer TMDCs significantly enhances interstitial electron localization, transforming weak intrinsic electride behavior into active catalytic sites that lower the HER overpotential.
- Tuning defect density and electron occupancy—via methods like doping or gating—enables dynamic optimization of the electride state, paving the way for on-demand, high-efficiency catalysts in energy conversion applications.

Acknowledgements

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