COMPUTATIONAL DESIGN

Hydrogen from the chalcogen hole

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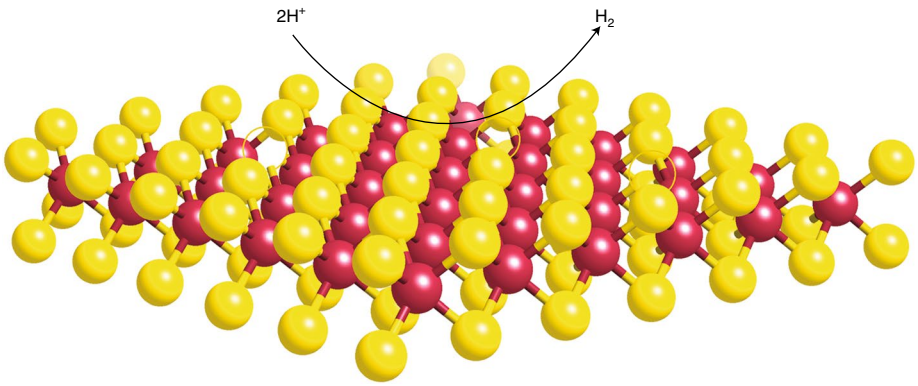

The electrochemical generation of hydrogen has been in the spotlight for decades as hydrogen is set to become an important source of fuel in the future. Despite being usually coupled with the oxygen evolution reaction in a water electrolyser, the hydrogen-evolution reaction (HER) can also be paired with other reactions — such as alcohol oxidative upgrading, to name an example — to circumvent the sluggish kinetics of evolving oxygen. Platinum is still the most prominent catalyst for this reaction, though some alternatives are starting to emerge that may soon replace this scarce and expensive precious metal. Two-dimensional transition metal dichalcogenides (TMDCs), with molybdenum disulfide as its most well known example, have been attracting a lot of attention as viable, inexpensive alternatives to platinum. It is well established that edge sites are the catalytically active sites of TMDC, as opposed to the more desirable but nearly inert basal plane sites. However, it was recently shown that the precise control of chalcogen vacancies also results in highly active hydrogen evolution basal plane sites.

Now, Seungwu Han, Youngho Kang and colleagues present a systematic computational study to explore the limits of chalcogen-vacancy-containing TMDCs as hydrogen evolution catalysts. The work is comprised of the combination of 17 transition metals and a chalcogen (S, Se, Te) in their most stable crystalline phase. The Gibbs free energy of adsorption of a single hydrogen atom is taken as the activity descriptor that correlates with the exchange current by a volcano-shaped function, as commonly established for electrocatalytic hydrogen evolution predictions. Three different basal plane sites are considered, including the stoichiometric surface and two different concentrations of chalcogen vacancies.

Various vacancy-containing TMDCs are predicted to exhibit excellent performance towards the HER, even outperforming MoS_{2-x} and approaching that of platinum, such as $ZrSe_{2-x}$, $ReTe_{2-x}$ or WSe_{2-x}. The Gibbs free energy of adsorption of hydrogen is well described by a multivariable function that contains the vacancy formation energy and the TMDC frontier orbitals' energy. It is finally suggested that, for the most active TMDC, there is an optimum vacancy content that maximizes the HER activity approaching the theoretical limit at moderate vacancy concentrations — within 6–25% — as previously demonstrated by others for MoS_{2-x}. This work should inspire experimentalists working in the field to test out the predicted findings.

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