

# Tuning the chemical reactivity of layered metal chalcogenides: the cases of PtTe<sub>2</sub> and InSe

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The capability to control the binding energy of adsorbed molecules on solid surfaces is crucial for the design of innovative catalysts. By introducing active sites, the catalytic activity can be significantly modified, up to transform non-reactive materials into selective and efficient catalysts. By combining experiments and density functional theory, we examined different channels through which chemical reactivity can be tuned in layered metal chalcogenides. Here, we will discuss two case-study examples: PtTe<sub>2</sub> and InSe.

PtTe<sub>2</sub> is a transition-metal dichalcogenide hosting type-II Dirac fermions [1], which displays application capabilities in optoelectronics [1] and hydrogen evolution reaction [2]. We demonstrate that the pristine surface of PtTe<sub>2</sub> is chemically inert toward the most common ambient gases (oxygen and water) and even in air. The creation of Te vacancies leads to the appearance of tellurium-oxide phases upon exposing defected PtTe<sub>2</sub> surfaces to oxygen or ambient atmosphere, which is detrimental for the ambient stability of uncapped PtTe<sub>2</sub>-based devices [4]. On the contrary, in PtTe<sub>2</sub> surfaces modified by the joint presence of Te vacancies and substitutional carbon atoms, we observe by the stable adsorption of hydroxyl groups,

that is an essential step for water splitting and the water–gas shift reaction.

Another powerful tool to tune the chemical reactivity of a layered material is related to its exfoliation in atomically thin layers, as we explored for the case of InSe [4]. Defect-free bulk samples of InSe do not show chemical activity. However, the presence of Se vacancies makes the decomposition of water molecules energetically favourable. In principle, few layers of InSe should present more active sites compared to its bulk counterpart. Accordingly, we produced single- and few-layer InSe nanosheets by liquid-phase exfoliation of β-InSe single crystals in 2-propanol. The potentiality of exfoliated-InSe as catalyst for hydrogen evolution reaction (HER) is tested into single-walled carbon nanotubes/InSe heterostructures. HER-overpotentials of 549 mV at pH = 1 and 451 mV at pH=14 are obtained using InSe nanosheets, outperforming their bulk counterpart. To unveil the origin of the catalytic efficiency of InSe nanosheets, we have built a theoretical model, which correlates the catalytic activity mainly to the Se vacancies in the InSe nanosheets. Specifically, we find a reduced exothermic differential Gibbs energy ΔG in the defected InSe monolayer in comparison with its pristine counterpart. The effects of bending and rippling of InSe flakes on catalysis are also theoretically assessed. These results pave the way for the use of InSe nanosheets in water splitting and for further optimization as flexible (photo-)electrocatalyst.

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## References

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