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Water splitting at two-dimensional carbon-based materials

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Two-dimensional materials often exhibit unique electronic properties that are promising for applications in electronic devices, and they are well-suited for catalysis due to their high surface areas. In particular, using sunlight or other renewable sources to photo- or electrocatalyze the water splitting reaction at these materials may provide a significant contribution to a sustainable energy infrastructure.
Here, we present density functional theory (DFT) investigations on two example materials that have been used to catalyze the hydrogen evolution reaction (HER). The first group are MXenes, specifically Ti3C2 and V2C [1]. They show some HER activity on their own, but can also be used as support materials for rhodium atoms, which leads to HER rates that rival those of platinum catalysts. Our calculations suggest that the Rh atoms are partially oxidized, and that the degree of hydroxylation strongly affects the hydrogen adsorption energy and, consequently, the HER activity. Adsorption switches from strongly exothermic to endothermic with increasing hydroxyl coverage, providing an intermediate region in which the hydrogen binding hits the sweet spot for efficient catalysis.
The second example are covalent organic frameworks (COFs), which consist of molecular building blocks which are connected in two-dimensional networks. Varying the building blocks and their connectivity, for example by considering different constitutional isomers of imine-linked COFs, leads to a large variation in HER activity [2]. Our calculations revealed that hydrogen adsorption energies of the two isomers are rather similar, but solvent effects and differences in the charge distribution upon hydrogen adsorption may play a large role for the observed activity differences. [3]

References:
[1] A. S. Zverev, C. Penschke, L. Cancellara, S. Reinicke, C. Günter, S. Rüstig, N. Deepak, S. Kogikoski Jr, P. Saalfrank, and I. Bald, Small 22, e10349 (2026).
[2] J. Yang, S. Ghosh, J. Roeser, A. Acharjya, C. Penschke, Y. Tsutsui, J. Rabeah, T. Wang, S. Y. Djoko Tameu, M.-Y. Ye, J. Grüneberg, S. Li, C. Li, R. Schomäcker, R. Van De Krol, S. Seki, P. Saalfrank, and A. Thomas, Nat. Commun. 13, 6317 (2022).
[3] F. Gottwald, C. Penschke, and P. Saalfrank, Phys. Chem. Chem. Phys. 26, 21821–21831 (2024).