Exploring the Flatland of 2D materials by electrochemical STM: visualization of the active sites for the hydrogen evolution reaction with atomic scale precision

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2D materials such as chemically modified graphenes, transition metal dichalcogenides, layered double hydroxide to name only a few, are having a huge impact on electrocatalysis providing materials with outstanding activity for a variety of reactions.[1] However, despite the intense research efforts in this field, a clear identification of the real active sites in many reactions remains a great challenge, given the necessity to employ spatially and structurally sensitive techniques in *operando conditions* (i.e. during the application of an electrochemical potential in the presence of an electrolyte). Recently, we have developed an innovative approach to the study of 2D materials by using electrochemical Scanning tunneling microscopy. As demonstrated by a seminal paper,[2] this technique allows identifying catalytic processes at the nanoscale by observing a typical noise in the tunneling current, which is due to instantaneous variations of the tunneling junction. Starting from here, we have introduced a new quantity, the tunneling current roughness, which allowed us to acquire quantitative measurements of the electrocatalytic activity with subnanometric precision.
By using special model systems consisting of CVD grown transition metal dichalcogenides thin films ($MoSe_2$ and WSe_2), and iron ultrathin films covered by graphene, we achieved even atomic resolution in *operando* during the hydrogen evolution reaction. This allowed us to identify and quantitatively compare the chemical activity of several chemical and morphological features such as single atom vacancies, Fe-C4 defects, step edges, and even exotic line defects such as metallic twin boundaries.[3] In particular we could determine that iron single atoms trapped within the graphene basal plane are even more active than platinum, the benchmark catalyst for the hydrogen evolution reaction.

References

[1] Chia, X., Pumera, M. Nature Catalysis 10 (2018) 909-921
[2] Pfisterer, J.H., Liang, Y., Schneider, O. Bandarenka, A.S., Nature, 549 (2017) 549, 74.
[3] Kosmala, T., H. Coy-Diaz, Komsa, H.-P., Ma. Y., Krasheninnikov, A., Batzill, M. Agnoli S. Advanced Energy Materials (2018) 180031