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Probing Nanoscale Heterogeneity in HER Activity of Mo₂C Catalysts via Scanning Electrochemical Cell Microscopy: Insights into Native Oxide Effects

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Strategies to enhance a catalysts' electrochemical activity are based on precise material design. This study presents a comprehensive analysis of doping 2D materials with transition metals (TMs)¹, combining theoretical predictions with experimental investigation to elucidate the impact of doping on electronic and electrochemical activity. Focusing on a MoS₂ monolayer, we investigated the coordination of some 3d TM atoms using a combination of Density Functional Theory (DFT) simulations and scanning probe microscopies, notably Scanning Electrochemical Cell Microscopy (SECCM)². Our systematic exploration, particularly on Ti- and Ni-doped MoS₂ monolayers, centered on hydrogen evolution as probe reaction. SECCM measurements revealed heterogeneous changes in MoS₂ basal plane electrochemical activity upon Ti doping, contrasting with homogeneous decreases observed for Ni doping. Local point of zero charge (PZC)³ by SECCM measurements and Kelvin Probe Microscopy (KPM) images supported these findings, indicating a decrease in MoS₂ work function upon Ti doping, consistent with DFT simulations. KPM surface potential images suggested that Ti coordination on MoS₂ is more favorable in regions with higher surface potential, elucidating the observed heterogeneity in Ti-MoS₂ SECCM mapping and implying a more ionic interaction between Ti and the MoS₂ surface. Conversely, Ni coordination occurred across the entire flake surface, regardless of the initial surface potential. These findings underscore TM coordination as an effective, minimally invasive method for doping 2D materials, augmenting their electrochemical activity at the basal plane. Variations in electrochemical behavior offer avenues for tailored design and optimization of 2D materials, promising advancements in various electrocatalytic processes. Acknowledgments Alexander von Humboldt Foundation (88881.699096/2022-01), CAPES, CNPq (400755/2022-0), FAPERJ (E-26/210.296/2022), Serrapilheira Institute (R-2012-37959), INCT/Nanocarbono, and European Research Council (No. 101046742 - MeBattery) funding are gratefully acknowledged. References 1. Liu, H. et al. 3d transition metal coordination on monolayer MoS₂: a facile doping method to functionalize surfaces. *Nanoscale* 14, 10801–10815 (2022). 2. Santana Santos, C., Jaato, B. N., Sanjuán, I., Schuhmann, W. & Andronescu, C. Operando Scanning Electrochemical Probe Microscopy during Electrocatalysis. *Chem. Rev.* 123, 4972–5019 (2023). 3. Kim, M. et al. Acidic Hydrogen Evolution Electrocatalysis at High-Entropy Alloys Correlates with its Composition-Dependent Potential of Zero Charge. *Angew. Chem. Int. Ed.* 62, e202310069 (2023).