Highlights

RESEARCH AREA 1 - Superconductors and Innovative materials for Energy and Environment - 2024

On the origin of the improved hydrogen evolution reaction in Mn- and Co-doped MoS_2

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NANOSCALE

In the field of hydrogen production, MoS_2 demonstrates good catalytic properties for the hydrogen evolution reaction (HER) which improve when doped with metal cations. However, while the role of sulfur atoms as active sites in the HER is largely reported, the role of metal atoms (i.e. molybdenum or the dopant cations) has yet to be studied in depth. To understand the role of the metal dopant, we study MoS_2 thin films doped with Co and Mn ions. We identify the contribution of the electronic bands of the Mn and Co dopants to the integral valence band of the material using in situ resonant photoemission measurements. We demonstrate that Mn and Co dopants act differently: Mn doping favors the shift of the S–Mo hybridized band towards the Fermi level, while in the case of Co doping it is the less hybridized Co band that shifts closer to the Fermi level. Doping with Mn increases the effectiveness of S as the active site, thus improving the HER, while doping with Co introduces the metallic site of Co as the active site, which is less effective in improving HER properties. We therefore clarify the role of the dopant cation in the electronic structure determining the active site for hydrogen adsorption/desorption. Our results pave the way for the design of efficient materials for hydrogen production via the doping route, which can be extended to different catalytic reactions in the field of energy applications.

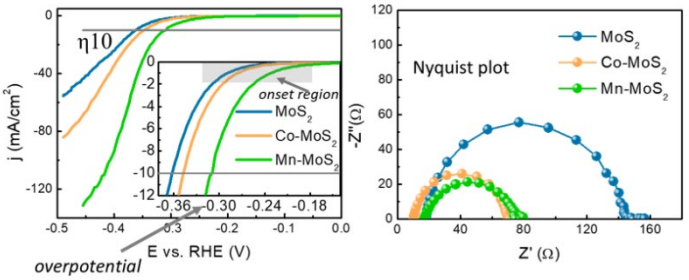

Fig. 1: Electrochemical impedance spectroscopy measurements. (left panel) Linear sweep voltammograms corrected by the potential drop iR. The arrows indicate the onset potential with current density > 1 mA cm^{-2} and the overpotential with current density > 10 mA cm^{-2}. (right panel) Nyquist plots obtained from the imaginary and real parts of the complex impedance.

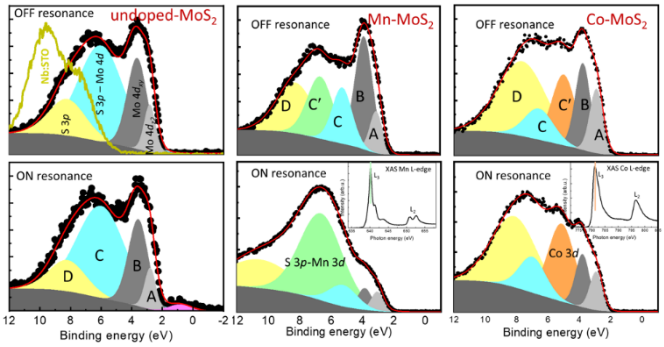

Fig. 2: Resonant photoemission spectroscopy results together with a multicomponent fit of the valence band. (left panel) Mo $M_{2,3}$-edge of undoped MoS_2 sample; (center panel) off resonance measurements on the top and on resonance on the bottom at the Mn $L_{2,3}$-edge of Mn-MoS_2 sample; (right panel) off resonance measurements on the top and on resonance on the bottom at the Co $L_{2,3}$-edge of Co-MoS_2 sample.

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