

Correlation between electronic properties and surface reactions of doped and undoped MoS₂ films for hydrogen production

Carmela Aruta

CNR-SPIN, via del Fosso del Cavaliere 100, Roma 00133, Italy

carmela.aruta@spin.cnr.it

Transition metal dichalcogenides are gaining increasing importance in the field of energy applications. In particular, it is well known that MoS₂ exhibits interesting hydrogen evolution reaction (HER) properties for electrochemical water splitting. Despite the extensive research conducted, identifying which atomic sites are active, and how to optimize their effectiveness and quantity, remain widely debated for MoS₂. Sulfur atoms, particularly at edge sites rather than in-plane, are considered the main active sites for catalytic reactions on the MoS₂ surface. However, more recently, metal cations, including dopant cations, have been also considered as efficient active sites. [1], [2]

To understand the role of metal dopants, we studied MoS₂ thin films doped with Co and Mn ions by measuring the photoemission spectroscopy in resonance at the absorption edge of each metal cation. The contribution of the single electronic band to the integral valence band plays a different role depending on the doping state. 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. These band shifts can be correlated with improved catalytic properties in the order of MoS₂<Co-MoS₂<Mn-MoS₂ in the HER process. Mn doping enhances the effectiveness of S as the active site, thus improving the HER, while Co doping introduces the metallic Co site as the active site, which improves HER properties to a lesser extent. [3]

The role of Co ions as active sites is confirmed by in-situ ambient pressure X-ray absorption measurements in water vapour, showing that the HER improvement in the case of Co doping in MoS₂ can be attributed to the electron exchange of H with Co ions.

References

- [1] Y. Huang et al., J. Am. Chem. Soc., 137 (2015) 6692.
- [2] J. Staszak-Jirkovský et al., Nature Mater. 15 (2016) 197.
- [3] P. Orgiani et al., Nanoscale 16 (2024) 12237.

Figures

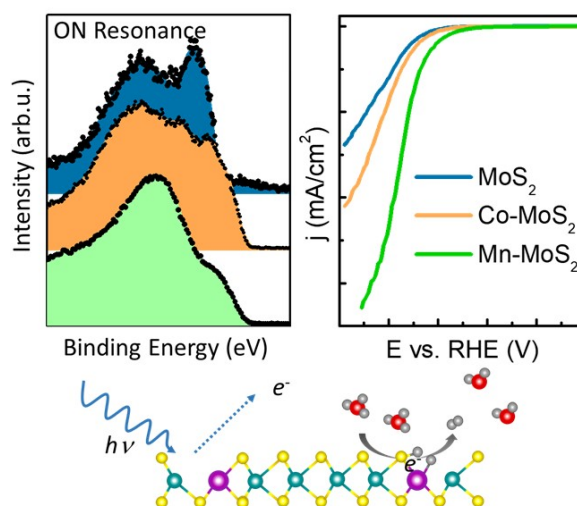


Figure 1: Photoemission spectroscopy on resonance at the absorption edge of each metal cation (Mo, Co and Mn) (left) and corresponding electrochemical results from linear sweep voltammograms (right) of undoped and doped MoS₂.