

Surface Coordination Chemistry of 2D Materials

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Two-dimensional materials (2DM) have attracted much interest due to their distinct optical, electronic, and catalytic properties. These properties can be tuned by various methods, including substitutional doping and, as recently demonstrated, surface functionalization with single atoms, thus increasing the 2DM portfolio. [1,2] This presentation will theoretically and experimentally describe the coordination reaction between MoS₂ monolayers with transition metals (TMs), exploring their nature and MoS₂-TMs interactions. Density Functional Theory calculations, X-Ray Photoelectron Spectroscopy, and Photoluminescence spectroscopy point to the formation of MoS₂-TM coordination complexes, where the adsorption energy for 3d TM resembles the crystal-field stabilization energy for weak-field complexes. Pearson's theory for hard-soft acid-base and Ligand-field theory discussed the periodic trends in 3d TM coordination on MoS₂ monolayer surfaces. We found that softer acids with higher ligand field stabilization energy, such as Ni²⁺, tend to form bonds with more covalent character with MoS₂, which can be considered a soft base.

On the other hand, harder acids, such as Cr³⁺ tend to form more ionic bonds. Additionally, we studied the trends in charge transfer and doping observed by XPS and PL results, where metals like Ni led to n-type doping. In contrast, Cu functionalization results in p-type doping. Therefore, the formation of coordination complexes on TMD's surface is a potentially effective way to control and understand the nature of single-atom functionalization of TMD monolayers without relying on or creating new defects.

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[1] H. Liu, D. Grasseschi, et al. Sci. Adv. 6 (2020) eabc9308. <https://doi.org/10.1126/sciadv.abc9308>.

[2] D. Grasseschi, et al. Coord. Chem. Rev. 422 (2020) 213469. <https://doi.org/10.1016/j.ccr.2020.213469>.