Vanadium Doped Transition Metal Sulfides for Enhanced Electrochemical Sensing and Catalysis

Transition metal sulfides (TMS) have shown great potential in electrochemical sensing and electrocatalysis due to their high surface area-to-volume ratio and reactive sulfur edge sites. Doping TMS with additional transition metals to alter their lattice and electronic structure can improve catalytic activity, analyte selectivity, and limit of detection (LOD) [1,2,3]. In this work, we investigate vanadium-doped MoS_2 at low concentrations (<9 at%) as an electrode material for electrochemical sensing and vanadium-alloyed WS_2 at high concentrations (x at%) as an efficient catalyst for the hydrogen evolution reaction (HER). To achieve low concentration doping, electrodeposition and thermal doping are utilized to synthesize the MoS_2 film and introduce tunable vanadium dopants, forming both vanadium single-atom catalyst (V-SAC) sites on the film surface and substitutional doping within the lattice. The presence of V-SACs has been previously confirmed through scanning transmission electron microscopy (STEM), while low vanadium content is verified via X-ray photoelectron spectroscopy (XPS) [2]. V-doped MoS_2 films synthesized on pyrolytic graphite sheets (PGS) and graphite paper (GP) demonstrate significant improvements in serotonin (SER) detection, with LODs of 500 nM on PGS and <4 μM on GP, compared to 5 μM for undoped MoS_2 on both substrates. To synthesize vanadium-alloyed WS_2, we employ a liquid precursor-assisted chemical vapor deposition (CVD) method, which enables tunable vanadium doping into the WS_2 lattice. At elevated doping levels in WS_2, localized domains of 2H-VS_2 form within the lattice, as evidenced by the emergence of 2H-VS_2 phonon modes in Raman spectroscopy. Raman mapping of highly doped flakes confirms that VS_2 is distributed predominantly along growth axes, causing highly variable local strain across the flakes. Scanning electron microscopy (SEM) further reveals surface inhomogeneities in flakes with high vanadium concentrations. Ongoing electrochemical measurements, including voltammetry and impedance spectroscopy, will be used to evaluate the V-doped TMS samples for their sensing and catalytic performance. Correlating electrochemical properties with doping levels will provide crucial insights for designing more efficient devices for prospective applications, such as wearable sensors and energy storage systems.

[1]Lei, Yu, et al. “Single-Atom Doping of MoS_2 with Manganese Enables Ultrasensitive Detection of Dopamine: Experimental and Computational Approach.” *Science Advances*, vol. 6, no. 32, Aug. 2020, p. eabc4250. *DOI.org (Crossref)*, https://doi.org/10.1126/sciadv.abc4250.

[2] Sun, Linxuan, et al. “Vanadium Single Atoms Embedded in MoS_2 Enabled Gut‐Brain Axis Neurotransmitter Detection at pM Levels.” *Small*, vol. 20, no. 39, Sept. 2024, p. 2307410. *DOI.org (Crossref)*, https://doi.org/10.1002/smll.202307410.

[3]Ruqia, Bibi, et al. “Catalyst Activation: Surface Doping Effects of Group VI Transition Metal Dichalcogenides towards Hydrogen Evolution Reaction in Acidic Media.” *Journal of Energy Chemistry*, vol. 72, Sept. 2022, pp. 217–40. *ScienceDirect*, https://doi.org/10.1016/j.jechem.2022.04.023.