# *P*-block metal monochalcogenides for $CO_2$ electroreduction *via* non-invasive van der Waals doping

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*P*-block metal monochalcogenides (MX) with black phosphorus-like structures are promising $CO_2$ reduction electrocatalysts due to their exposed metal sites and tunable electronics but face instability from lone-pair electron distortions and $CO_2$'s LUMO orbital mismatch. We propose a non-invasive van der Waals (vdW) doping strategy using misfit superlattices, combining MX with conductive transition metal dichalcogenide ($TX_2$) sublayers. Using $[BiS]_1[TaS_2]_1$ as a model, we show that vdW doping stabilizes BiS by adjusting Bi's valence to $Bi^{(2+\delta)}$ via ionic interactions and charge transfer, aligning Bi's *p*-orbital with $CO_2$'s LUMO to lower the activation barrier. DFT and in-situ studies confirm optimized Bi sites with strong *OCHO adsorption, achieving >90% formate selectivity and >110 $mA \cdot cm^{-2}$ partial current density at -1.1 V. HAADF-STEM and XPS verify $[BiS]_1[TaS_2]_1$'s high-purity, crystalline structure with excellent stability and exfoliability. Compared to $[SnS]_1[TaS_2]_1$ and $[PbS]_1[TaS_2]_1$, $[BiS]_1[TaS_2]_1$ excels in intrinsic activity. This vdW superlattice approach stabilizes p-block materials, tunes sublayer interactions, and enhances electrocatalytic efficiency for sustainable $CO_2$ conversion.

## References

[1] P. Li, et al. J. Am. Chem. Soc, (2025), 10.1021/jacs.5c03556.
[2] P. Li, et al. Adv. Energy Mater. 13 (2023), 2301597

## Figures

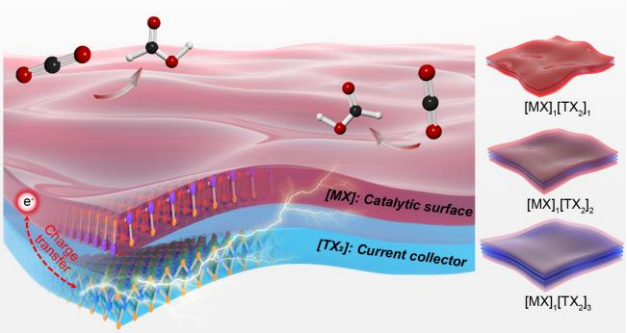


**Figure 1:** Non-invasive van der Waals doping in $[MX]_m[TX_2]_n$ misfit superlattices for enhanced $CO_2$ electroreduction.