

Supporting Information

2H $\rightarrow$ 1T Phase Transition and Hydrogen Evolution Activity of MoS₂, MoSe₂, WS₂ and WSe₂ Strongly Depends on the MX₂ composition

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Experimental Section

Materials

MoS₂, WS₂, MoSe₂ and WSe₂ bulk powder (< 2 μm), and *tert*-butyllithium (1.7M in pentane) were obtained from Aldrich, Czech Republic. Hexane was obtained from Lach-ner, Czech Republic. Argon (99.9999% purity) was obtained from SIAD, Czech Republic. Sulphuric acid (95-98%), *N,N*-dimethylformamide (DMF), and platinum on graphitized carbon (20 wt% Pt on Vulcano graphitized carbon) were purchased from Sigma–Aldrich, Singapore.

Apparatus

Voltammetric experiments were performed using a three-electrode configuration. A platinum wire served as an auxiliary electrode, while an Ag/AgCl wire served as a reference electrode. All electrochemical potentials in this paper are stated versus Ag/AgCl reference electrode. All voltammetric measurements were performed on a μAutolab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a personal computer and controlled by General Purpose Electrochemical Systems Version 4.9 software (Eco Chemie). X-ray photoelectron spectroscopy (XPS) was performed with a Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany). Both survey and high-resolution spectra for C1s were collected. Raman spectra were obtained by using a confocal micro-Raman LabRam HR instrument from Horiba Scientific in backscattering geometry with a CCD detector, a 514.5 nm Ar laser and a 100x objective mounted on a Olympus optical microscope. The calibration is initially made using a silicon reference at 520 cm⁻¹ and gives a peak position resolution of less than 1 cm⁻¹. Scanning Transmission Electron Microscopy (STEM) images were obtained by using Jeol 2100 TEM (Jeol, Japan) operating at 200 kV.

Procedures

Exfoliation of TMDs has been carried out by suspension of 3 g of the bulk powder in 20 ml of 1.7 M *t*-butyllithium in pentane. The solution has been stirred for 72 h at 25 °C under argon atmosphere. The Li-intercalated material has then been separated by suction filtration under argon atmosphere and the intercalation compound was washed several times with hexane (dried over Na). The separated TMD with intercalated Li was placed in water (100 ml) and repeatedly centrifuged (18 000 g). Obtained material was dried in vacuum oven at 50 °C for 48 hours prior the further use. Further characterization of the four TMD materials in the bulk state and after exfoliation is provided in supporting information (see Figures S5, S6 and S7 for XPS analysis).

Electrochemical measurements. Dispersions of all materials were prepared in *N,N*-dimethylformamide (DMF) at concentration of 5 mg/mL. 3 μL aliquot from each dispersion was deposited on a previously polished glassy carbon electrode (GC) and let it dry for about 20 min at

room temperature. Polarization curves to investigate catalytic abilities towards hydrogen evolution reaction (HER) were obtained in 0.5 M H_2SO_4 with scan rate of 2 mV/s.

Planar resistivity measurements were conducted by depositing 1 μL of the material suspension (prepared at 1 mg/mL concentration in water) onto the interdigitated electrode (Au-IDE) (width 10 μm ; spacing 5 μm). The electrode was then dried under a lamp for 30 min, leaving a randomly deposited material film on the interdigitated area bridging the two Au electrode bands. Resistivity (Ohm) vs frequency (Hz) curves were obtained applying an AC potential of 10 mV. Resistivity values for comparison were taken at the fixed frequency of 0.15 Hz.

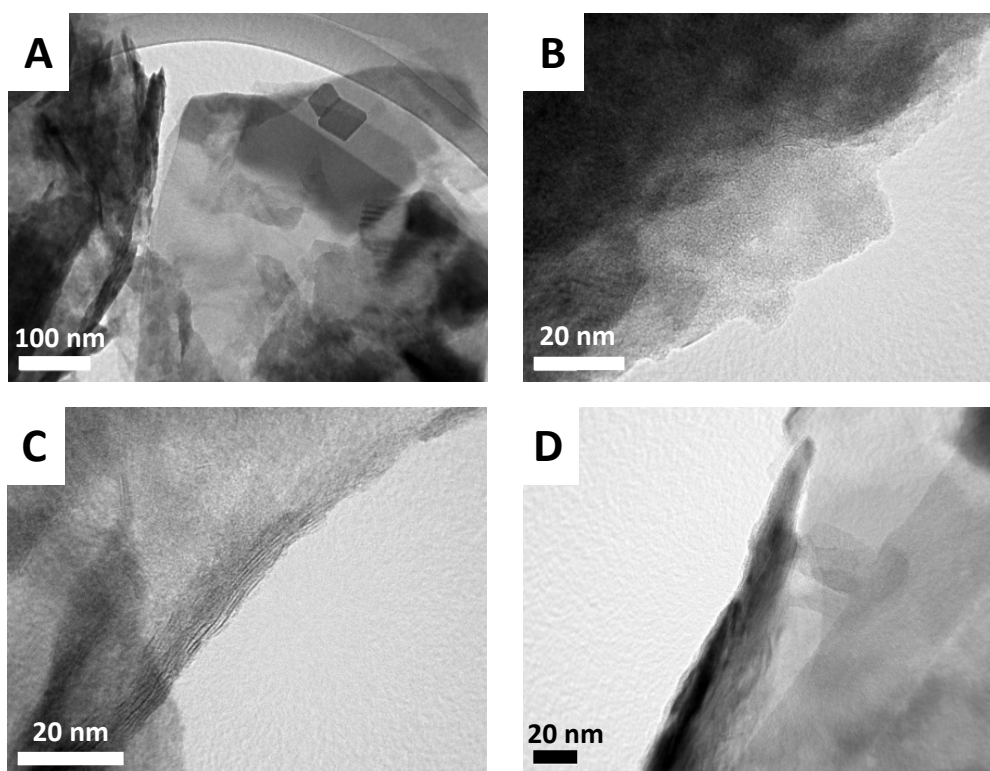


Figure S1. Low-resolution TEM pictures of A) MoS_2 , B) MoSe_2 , C) WS_2 and D) WSe_2 .

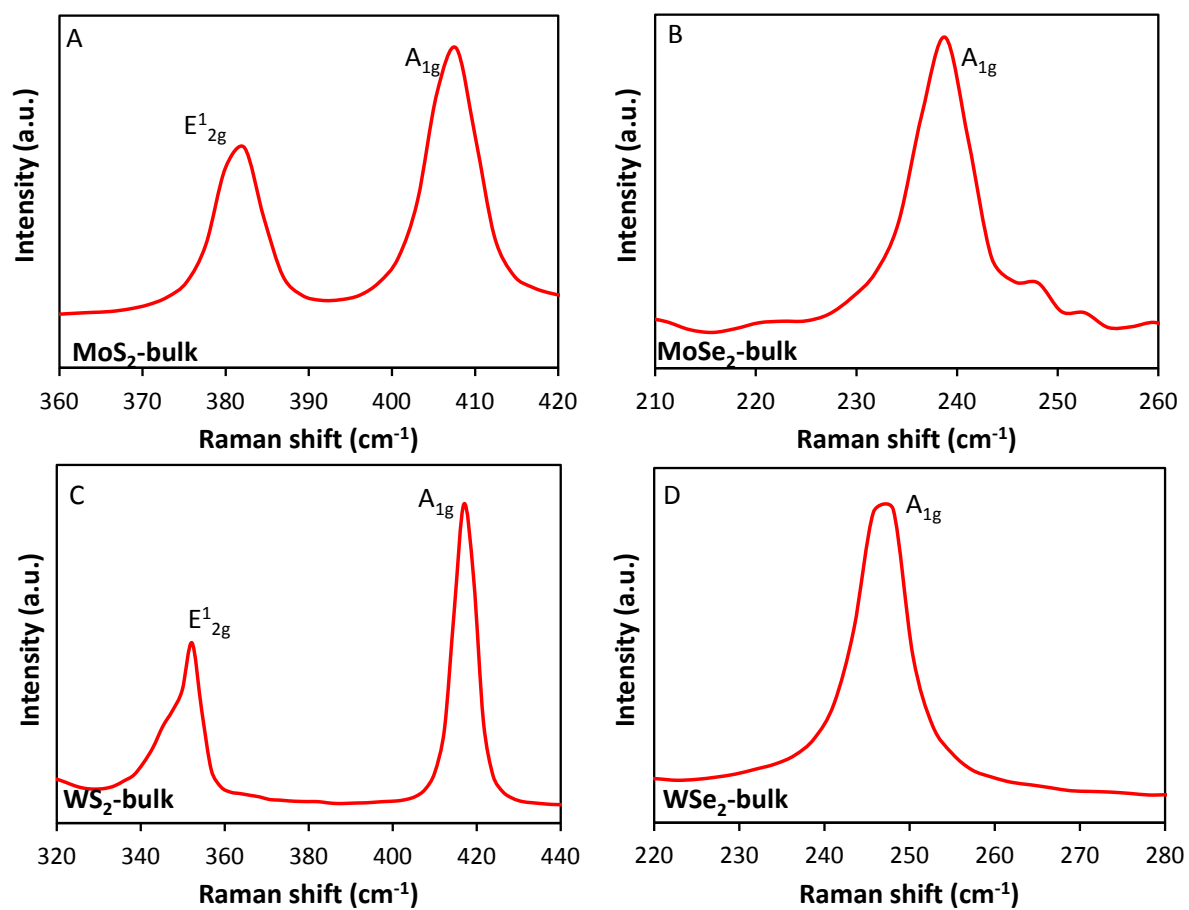


Figure S2. Raman spectra of bulk A) MoS₂, B) MoSe₂, C) WS₂ and D) WSe₂.

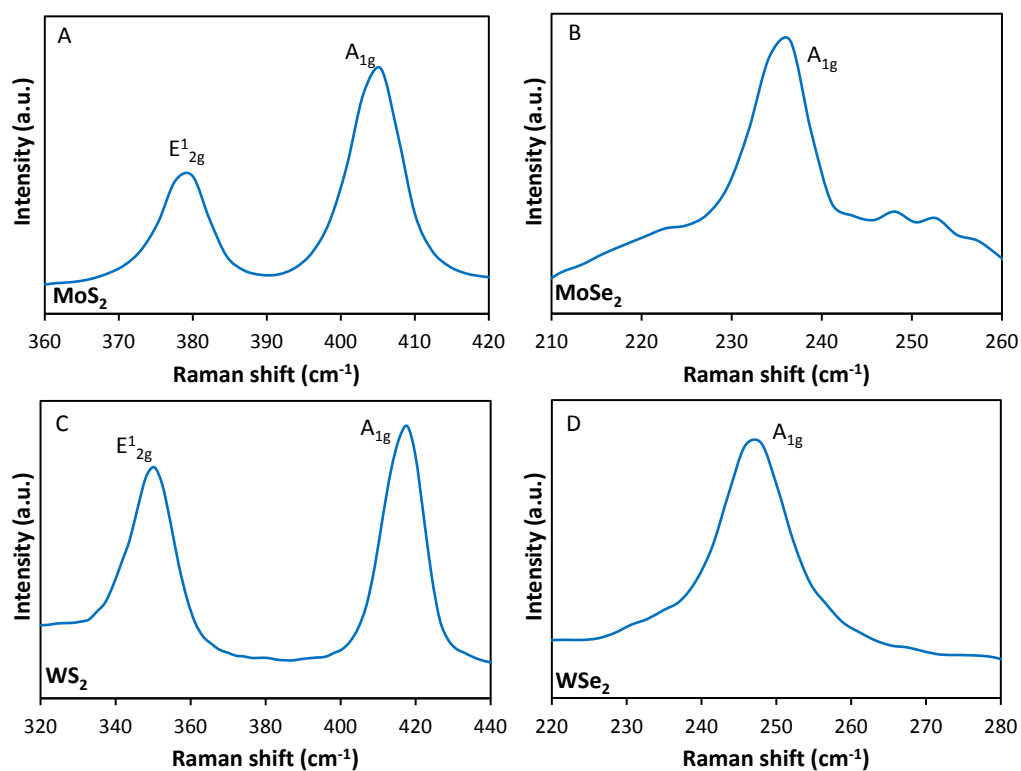


Figure S3. Raman spectra of exfoliated A) MoS₂, B) MoSe₂, C) WS₂ and D) WSe₂.

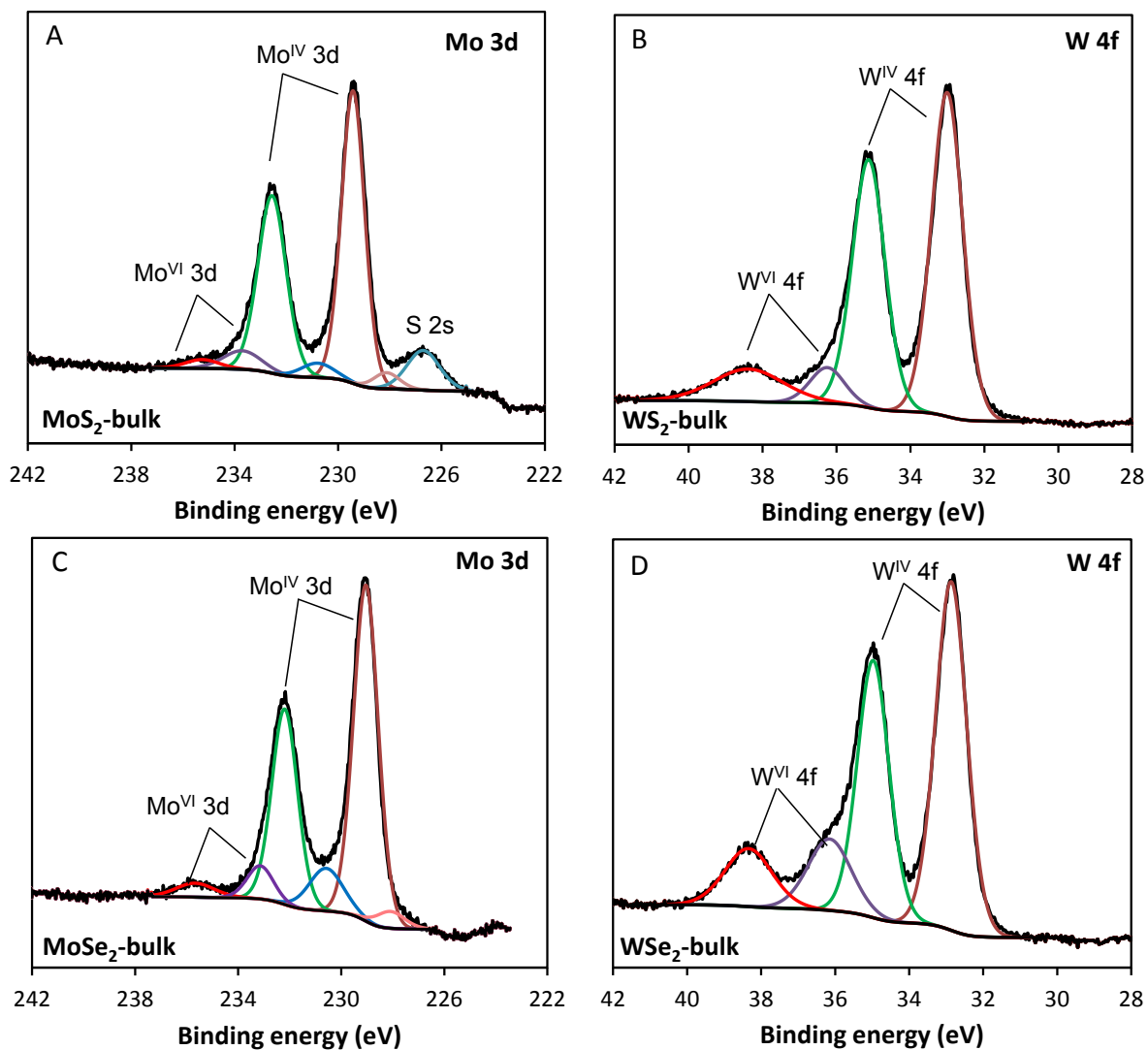


Figure S4. High-resolution XPS spectra of Mo 3d (left) and W 4f (right) for the bulk TMD materials.

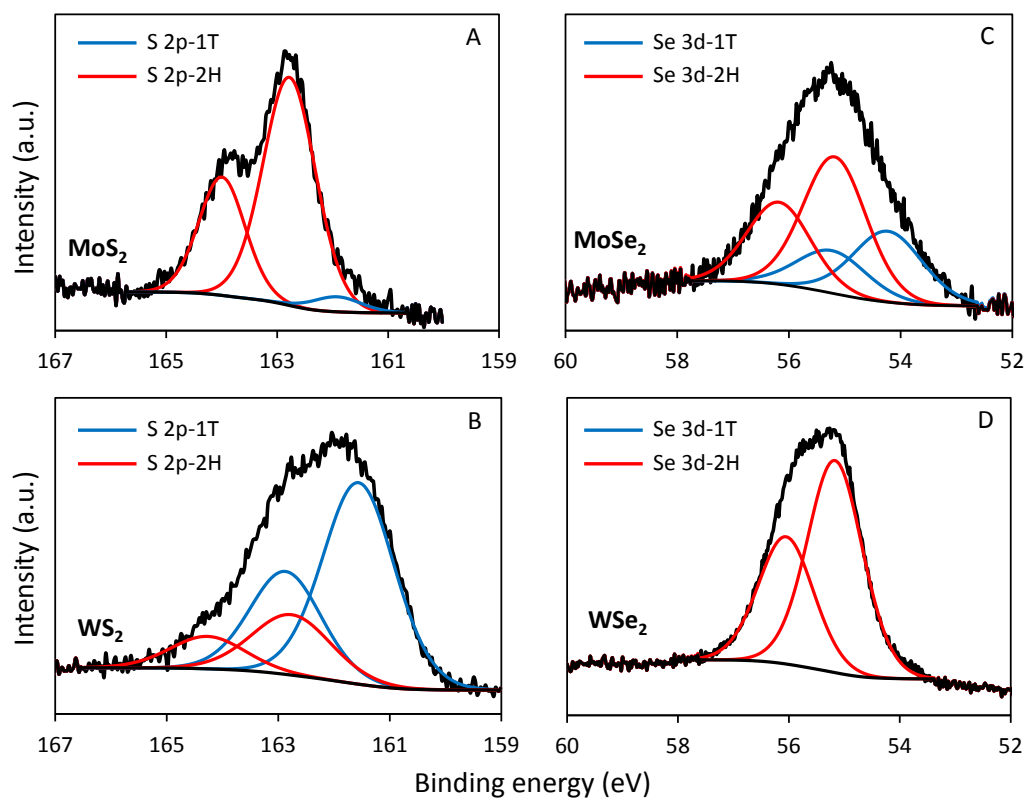


Figure S5. High-resolution XPS spectra of S 2p (left) and Se 3d (right) of exfoliated (A) MoS₂, (B) WS₂ (C) MoSe₂ and (D) WSe₂.

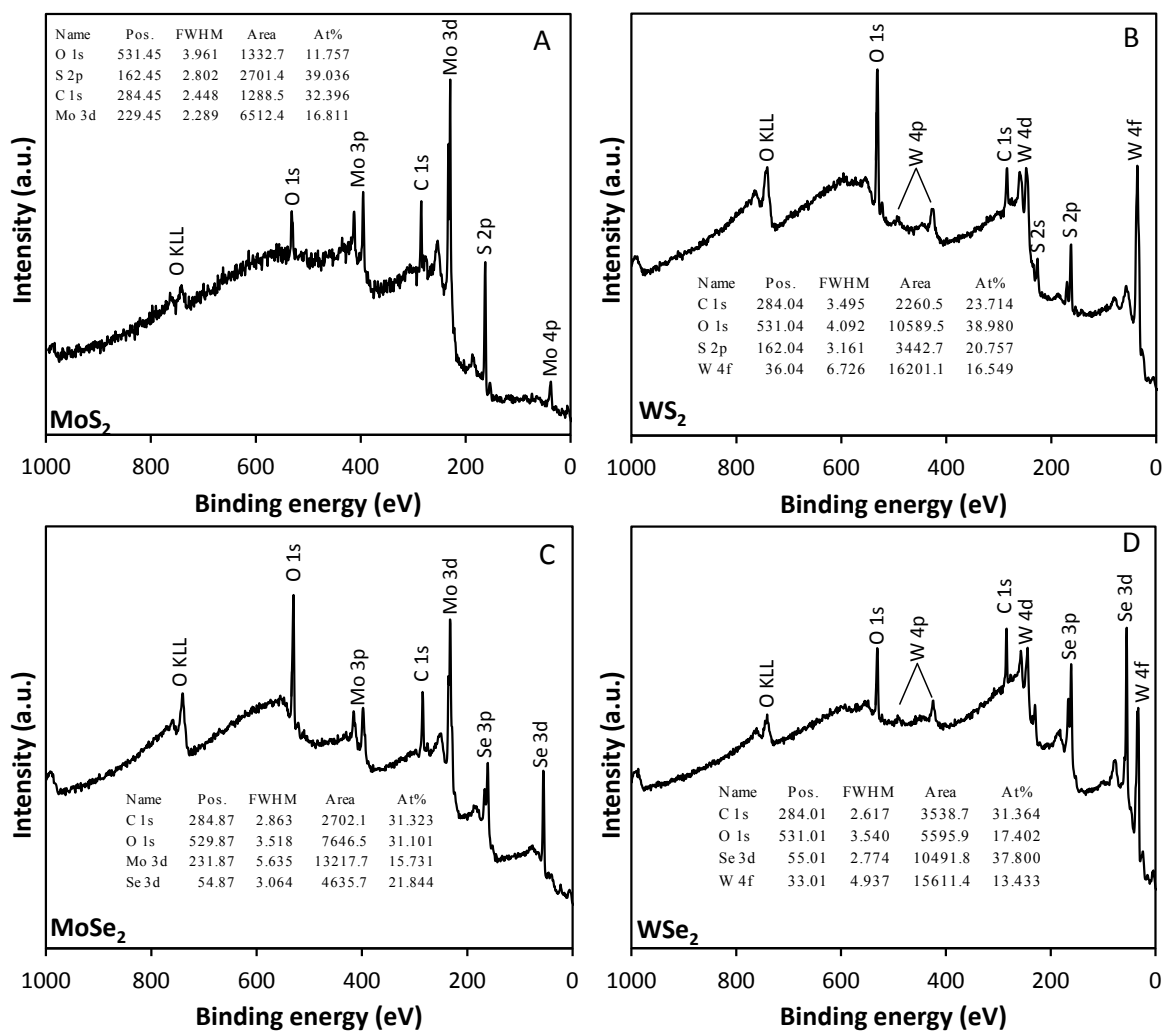


Figure S6. XPS wide spectra of exfoliated TMDs and atomic composition. (A) MoS₂, (B) WS₂ (C) MoSe₂ and (D) WSe₂.

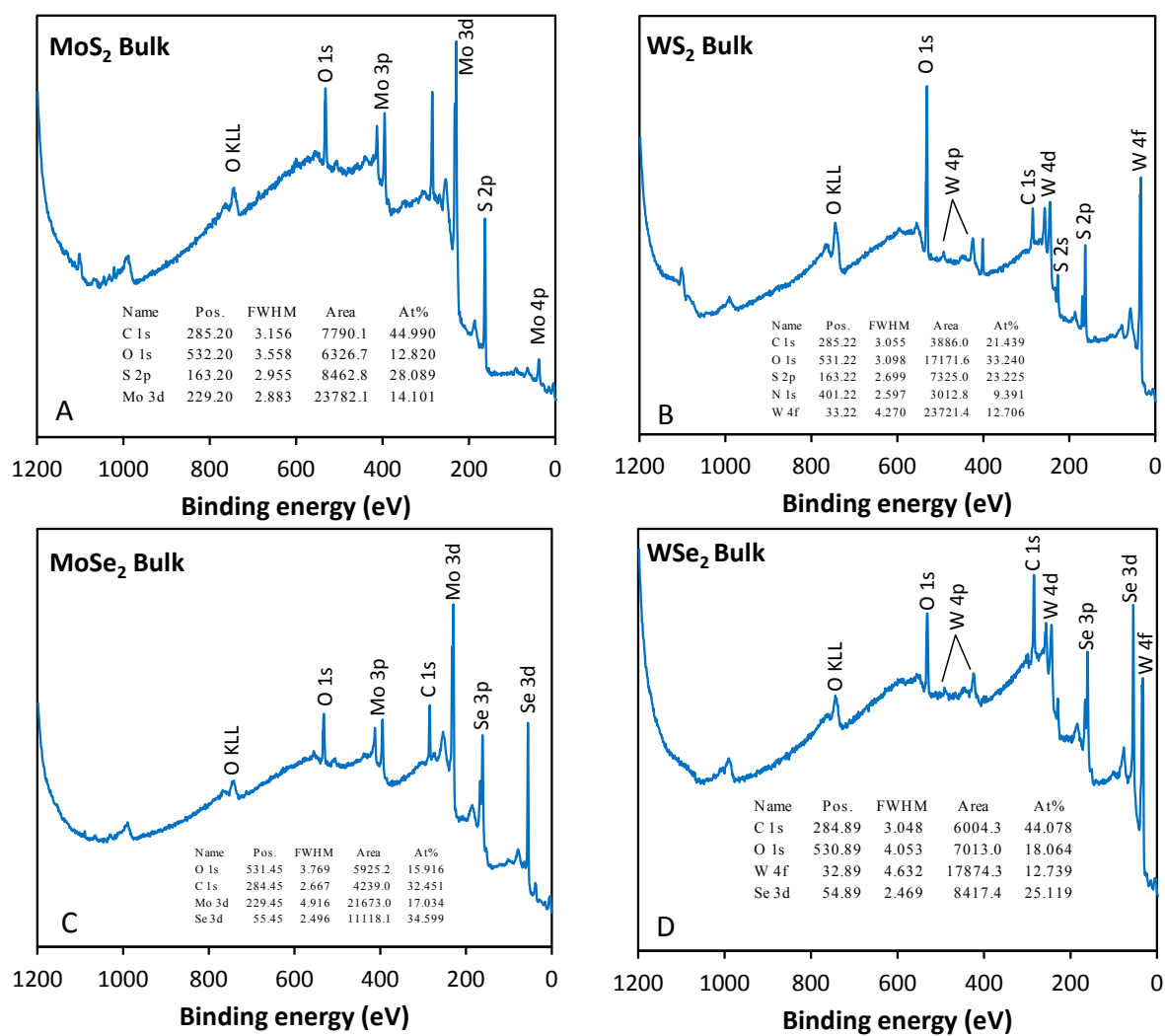


Figure S7. XPS wide spectra of bulk TMD materials. (A) MoS₂, (B) WS₂ (C) MoSe₂ and (D) WSe₂.

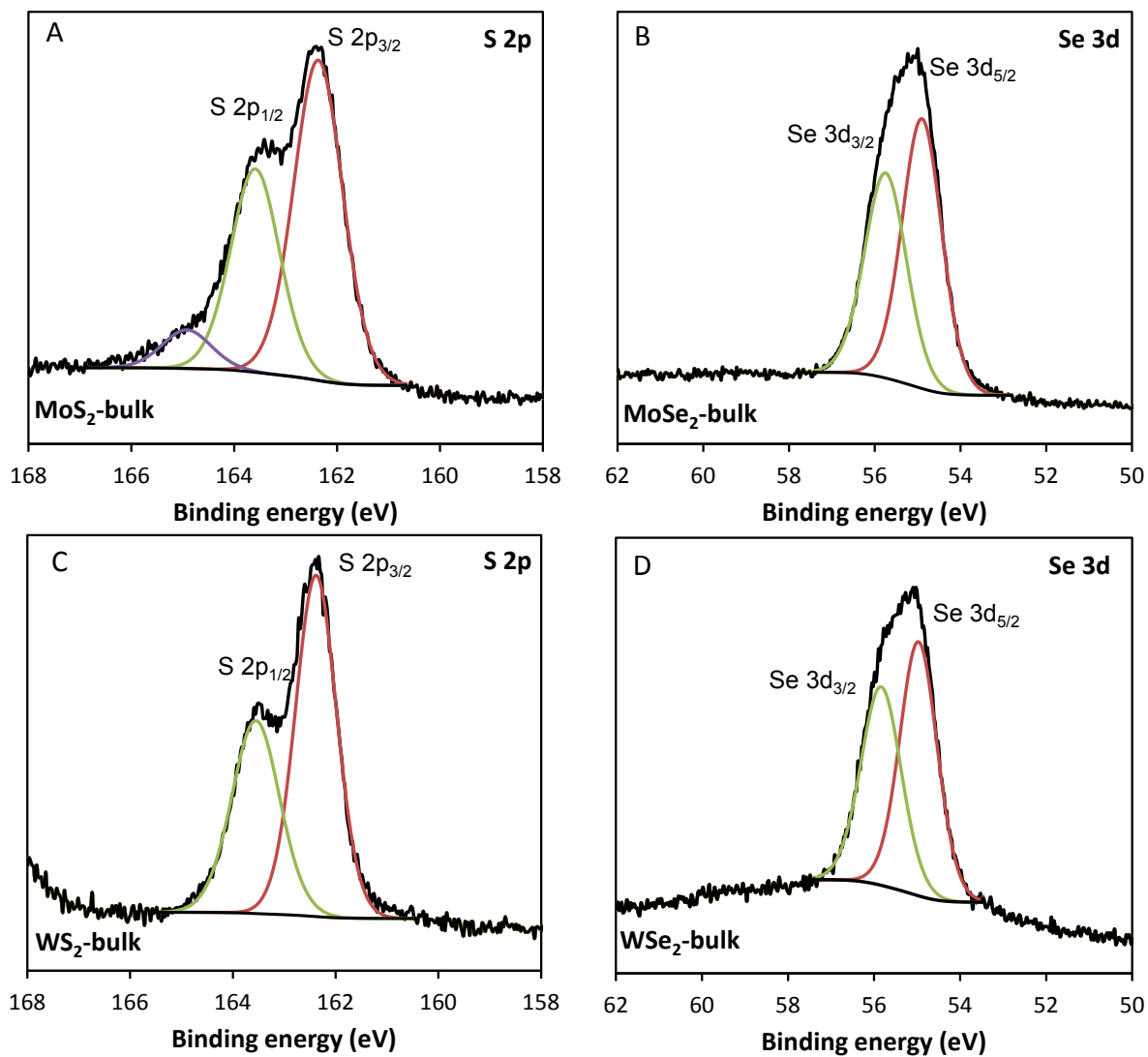


Figure S8. High-resolution XPS spectra of S 2p (left) and Se 3d (right) for the bulk TMD materials. (A) MoS_2 , (B) MoSe_2 (C) WS_2 and (D) WSe_2 .

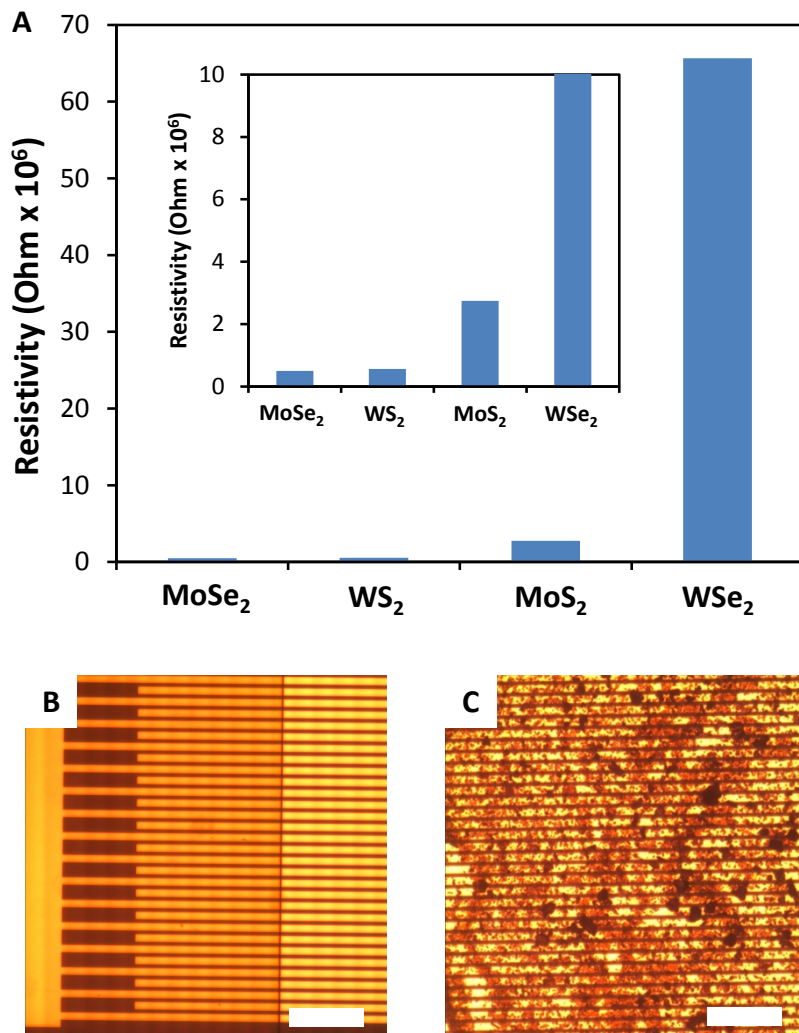


Figure S9. Planar resistivity of MoS₂, MoSe₂, WS₂ and WSe₂ (1 μ g) measured with an Au-IDE electrode (Width 10 μ m, spacing 5 μ m) applying an AC potential of 10 mV. **A)** Resistivity values taken at the frequency of 0.15 Hz. Picture of a section of the Au-IDE electrode before (**B**) and after (**C**) deposition of one TMD material. Scale bar corresponds to 100 μ m.

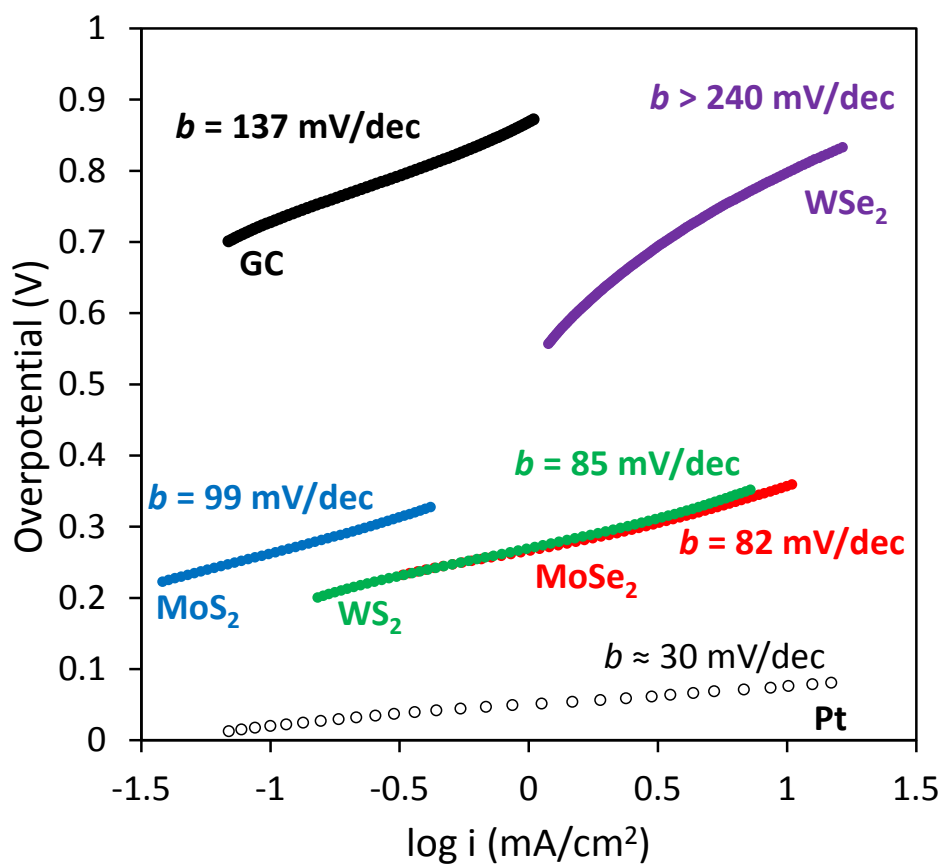


Figure S10. Tafel plots and corresponding slopes relative to the polarization curves in Figure 4.