Electronic Supplementary Material (ESI) for Materials Advances.

Single-crystalline WSe_2 Nanoflakes as Efficient Electrocatalysts

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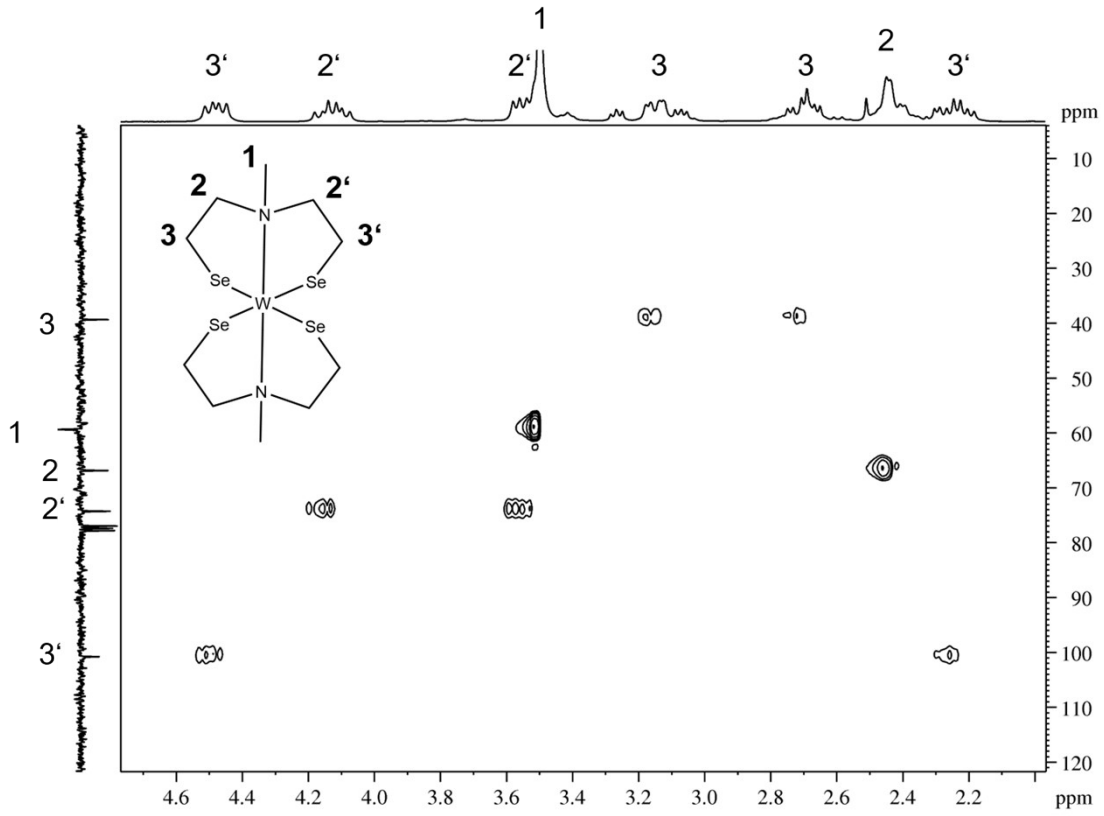
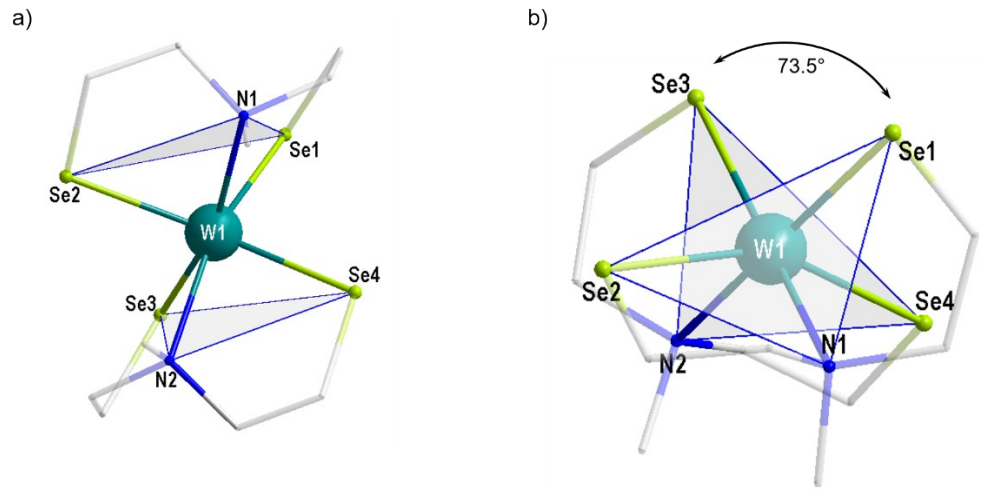
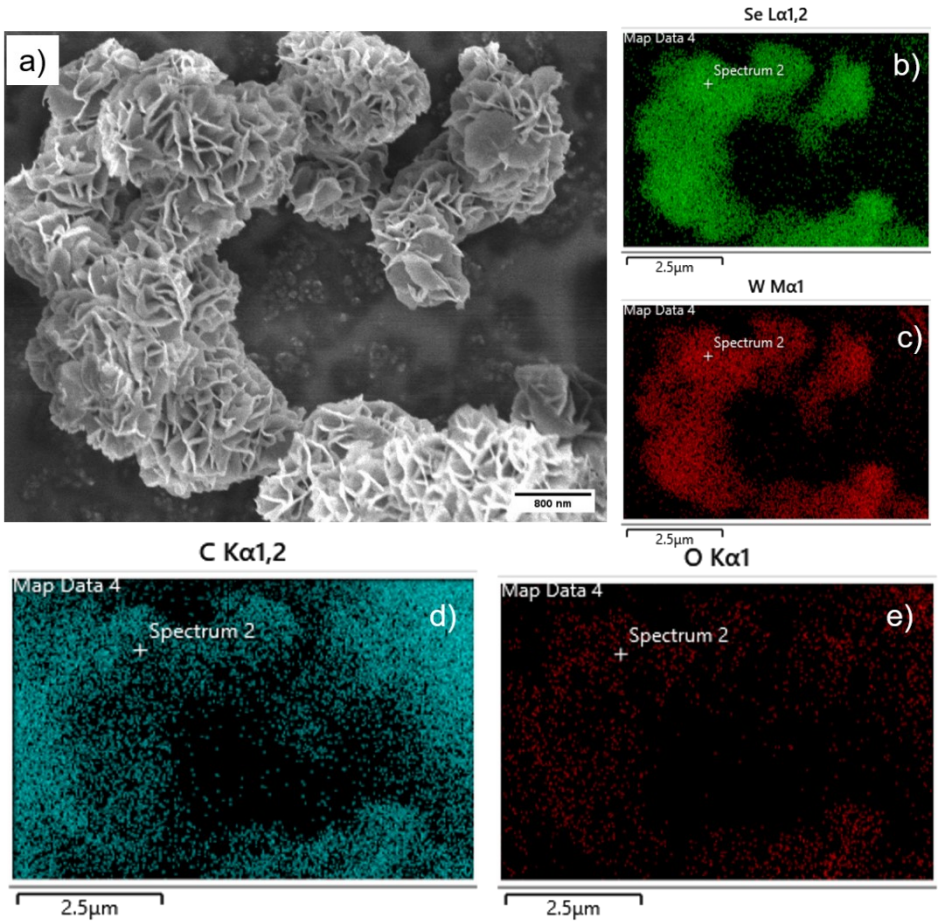


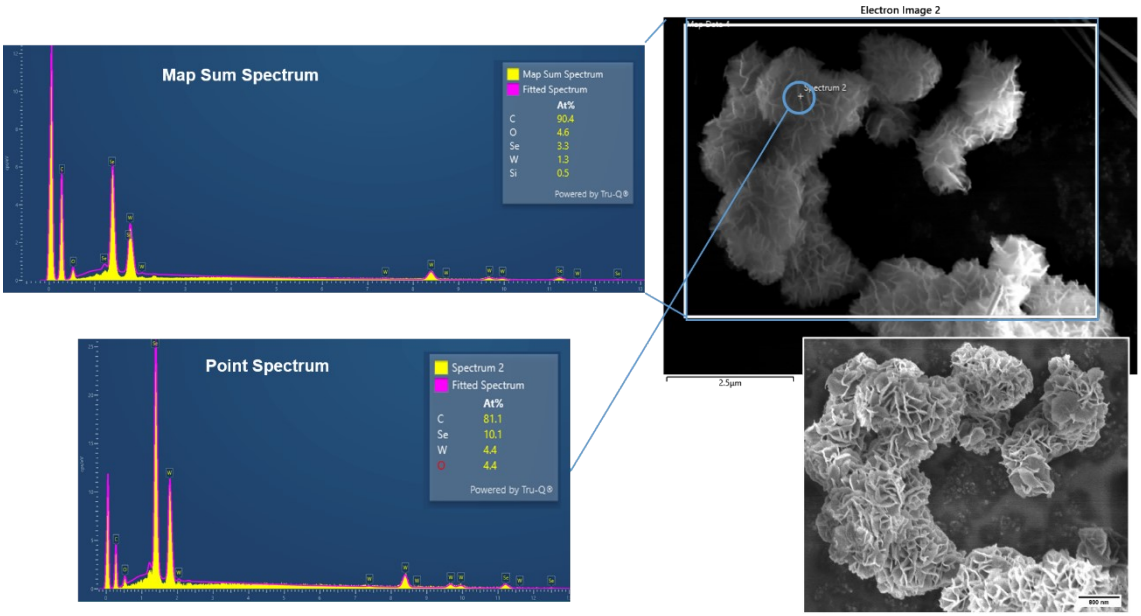
SI. Fig. 1: $^{1}H,^{13}C$ HSQC NMR spectrum with mapping of corresponding proton and carbon signals.



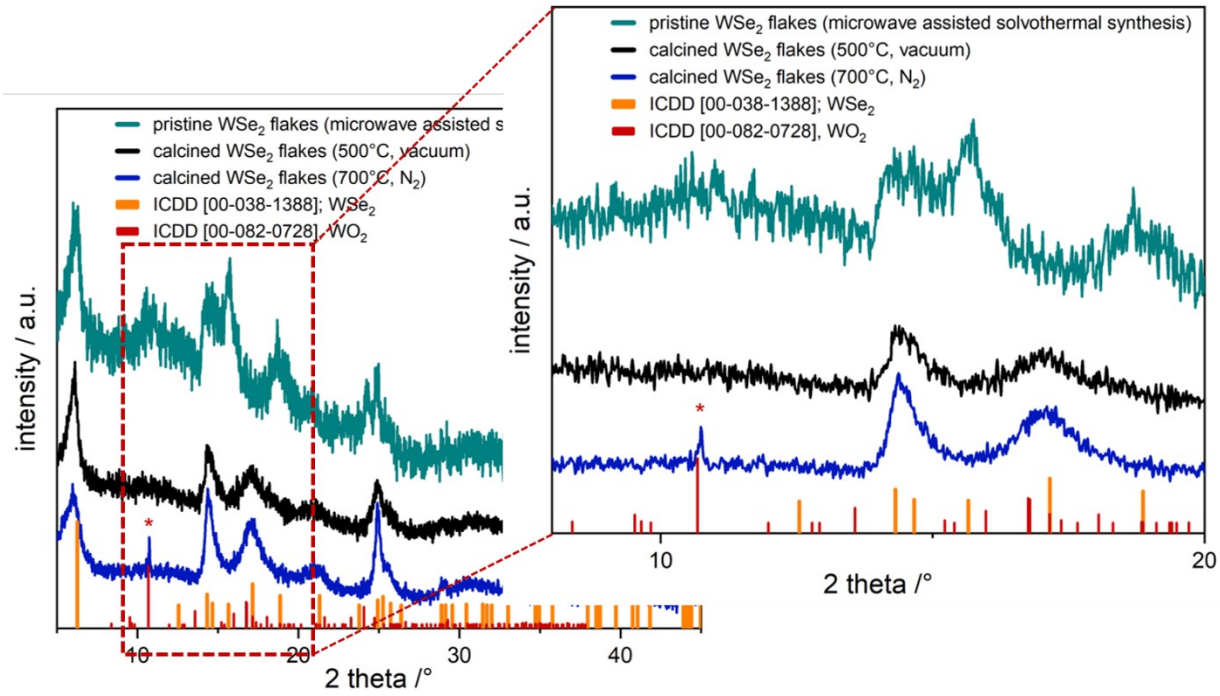
SI. Fig. 2: a) triangular planes of tridentate coordinated ligands and b) twist of formed planes.



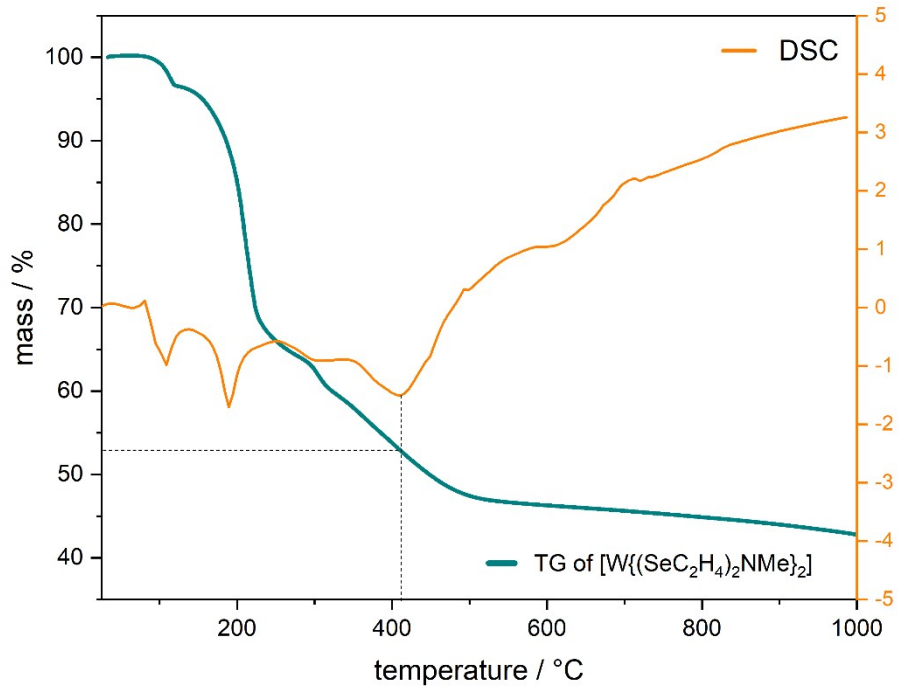
SI. Fig. 3: EDS mapping of as-produced WSe_2 flakes showing homogeneous distribution of W and Se (1:2 ratio). Furthermore, contamination of carbon was detected significantly, which may can come from contamination using ethanol to prepare the WSe_2 samples for SEM and EDS analysis or from remaining ligand fragments. Additionally, the oxygen contamination can come from the used solvent as well or from the substrate below (SiO_2).



SI. Fig. 4. EDS point mapping and Mag Sum Spectrum showing W : Se in a ratio of 1:2, confirming the formation of WSe_2.



*SI. Fig. 5: XRD pattern of fresh prepared WSe_2 flakes from microwave assisted solvothermal synthesis (pristine WSe_2; cyan pattern), calcined WSe_2 flakes in vacuum at 500°C (black pattern), calcined WSe_2 flakes at 700°C under N_2 atmosphere (blue pattern), orange reference of WSe_2 (ICDD 00-038-1388), *labeled formation of peak which fits not to the formation of any W-Se crystalline phase (or elemental W or Se) and may could assume the formation of an WO_2 crystalline phase (red reference: ICDD 00-082-0728, WO_2). The slight oxygen contamination observed could not be avoided under the given experimental condition (calcination process at higher temperatures, 700°C for 7h). Calcination of as-produced WSe_2 2D flakes was performed to improve the analysis of WSe_2 material. The oxygen contamination observed after the calcination at 700°C for 7h therefor has no influence of the performance of tested WSe_2 2D flakes.*



SI. Fig. 6: TG-DSC-Analysis of molecular precursor [W{(SeC$_2$H$_4$)$_2$NMe}$_2$] up to a temperature of 1000°C. TG Curve of molecular precursor presents in cyan, corresponding DSC curve presented in orange.

TG-Analysis of molecular precursor up to a temperature of 1000°C showed a multi-step decomposition. The decomposition starts at a temperature of around 85°C, which is indicated with an exothermic peak in DSC curve (orange), completing the first decomposition step at a temperature of around 100°C, which is indicated by an endothermic peak. In the following further endothermic decomposition steps at around 180°C and 300°C have been observed till the last endothermic peak in DSC curve at around 410°C fits to the theoretical calculated mass loss of 50% for the formation of pure WSe_2 (molecular precursor (M = 670.01 g/mol), pure WSe_2 (M = 341.78 g/mol) theoretic mass loss which fits to desired WSe_2 is indicated by black dotted lines). Continuous mass loss finished at around 500°C indicated by a weak exothermic peak in the DSC curve. In the temperature range from around 500°C – 1000°C continuous weight loss with increasing temperature, however without the formation of any plateau, revealing the limited stability at higher temperatures of these complex. The total weight loss of around 43% is rather too low to correspond with the formation of WSe_2. This behavior has been observed for isotype complexes of Hf and Zr before[1] and could may result from any partial oxidation of the decomposition product due to not fully inert conditions of the given experimental procedure. The detected total mass loss of around 43% fits also not to the complete oxidation of tungsten to WO_2 or WO_3, where may some mixed product have been formed or some partial sublimation of decomposition fragments has taken place.

[1] V. Brune, C. Hegemann, M. Wilhelm, N. Ates, S. Mathur, *Z. Anorg. Allg. Chem.* **2022**, *648*, e20220004.