Edge-site nano-engineering of WS_2 by low temperature plasma-enhanced atomic layer deposition for electrocatalytic hydrogen evolution

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Edge-enriched transition metal dichalcogenides (TMDs) like WS_2 are promising electrocatalysts for sustainable production of H_2 through the electrochemical hydrogen evolution reaction (HER). The reliable and controlled growth of such edge-enriched electrocatalysts at low temperatures has, however, remained elusive [1]. In this work, we demonstrate how plasma-enhanced atomic layer deposition (PEALD) can be used as a new approach to nano-engineer and enhance the HER performance of WS_2 by maximizing the density of reactive edge sites at a low temperature of 300 °C [2]. By altering the plasma gas composition from H_2S to H_2+H_2S during PEALD, we could precisely control the morphology and composition, and consequently, the edge-site density as well as chemistry in our WS_2 films. The precise control over edge-site density was verified by evaluating the number of exposed edge-sites using electrochemical copper underpotential depositions (Cu-UPD). Subsequently, we demonstrate the HER performance of the edge-enriched WS_2 electrocatalyst, and a clear correlation between plasma conditions, edge-site density and the HER performance is obtained. Additionally, using density functional theory (DFT) calculations we provide insights and explain how the addition of H_2 to the H_2S plasma impacts the PEALD growth behaviour, and consequently, the material properties, when compared to H_2S plasma only.

References

[1] Ho, T. A.; Bae, C.; Lee, S.; Kim, M.; Montero-Moreno, J. M.; Park, J. H.; Shin, H; Chem.Mater.,29 (2017) 7604-7614
[2] Balasubramanyam, S.; Shirazi, M.; Bloodgood, M.A.; Wu, L.; Vandalon, V.; Verheijen, M.A.; Kessels, W.M.M.; Hofmann, J.P.; Bol, A.A.; (2019-submitted to Chemistry of Materials Journal)

Figures

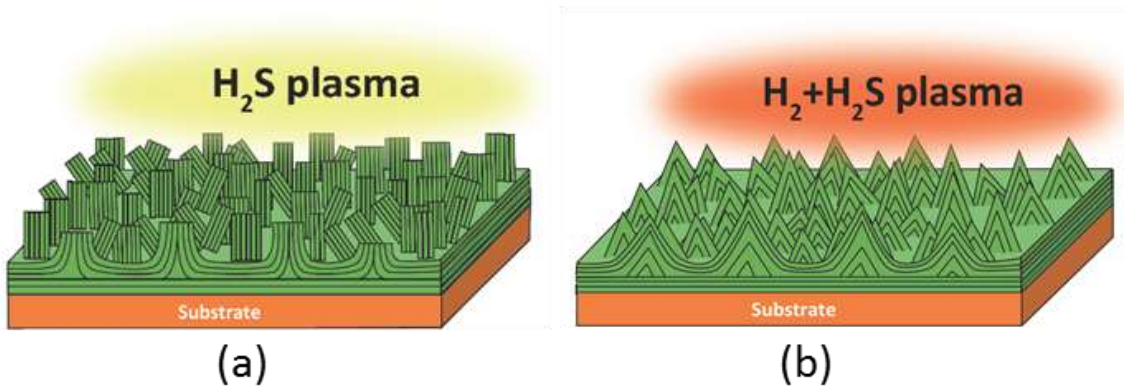

Figure 1: Schematic showing the morphological difference of WS_2 films synthesized by PEALD: (a) edge-terminated nanoflakes synthesized using H_2S plasma as co-reactant and (b) tapered, fin-like structures synthesized using H_2+H_2S plasma as co-reactant.