

Nanotubes and Nanostructures of VS_2 , WS_2 , and MoS_2 : Structural Effects on the Hydrogen Evolution Reaction

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Background

Vanadium disulfide (VS_2) emerges as a remarkable functional material, boasting myriad advantages that have propelled its widespread application across various industrial sectors. Its unique electronic and optical properties render it highly desirable for utilization in electronics, optoelectronics, and catalysis. Despite these advantages, the synthesis of VS_2 in specific morphologies, particularly as nanotubes, remains a significant challenge. The complexities associated with preparing various VS_2 nanostructures stem from the intricate control required over reaction conditions, precursor selection, and the delicate balance between promoting specific morphologies and preventing unintended structural transformations. This study aims to overcome these challenges in nanotube synthesis and unlock the full potential of VS_2 in cutting-edge technologies, promising advancements in diverse fields.

Methods

This study describes the preparation of novel VS_2 nanotubes with a unique structure, offering a comparative analysis with benchmark 2D materials MoS_2 and WS_2 . The unique VS_2 morphology was explored through electron tomography and compared with VS_2 nanoflowers. Catalytic activity of the various nanotubes and nanoflowers was measured, complemented by a Density Functional Theory (DFT) study to attain a fundamental understanding of the catalytic activity's origin in the materials system. Highly crystalline WS_2 nanotubes and nanotriangles, MoS_2 nanoflowers, and defect-rich MoS_2 nanotubes were synthesized and thoroughly studied for their Hydrogen Evolution Reaction (HER) activity. The synthesis of VS_2 nanostructures depended on the solvent and vanadium precursor, resulting in nanotubes and nanoflowers.

Results

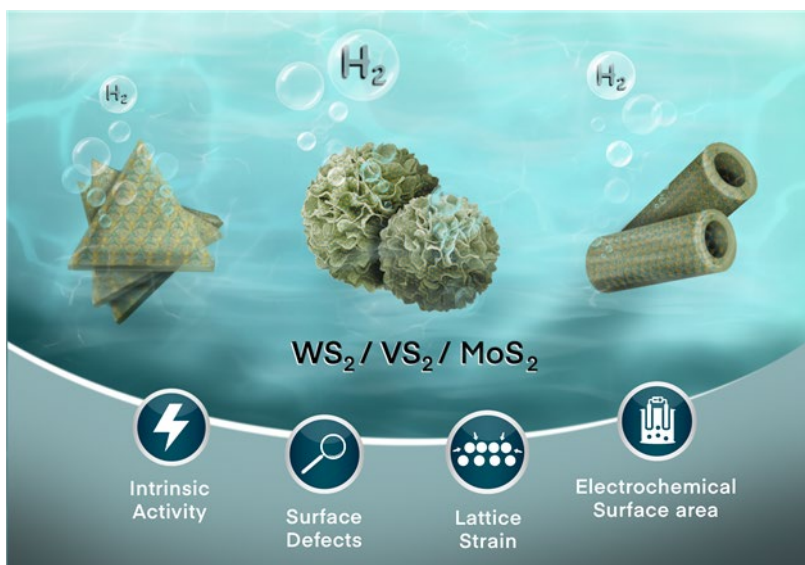
Characterization techniques, including TEM, SEM, powder X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), confirmed the structures' crystallinity and composition. Electron tomography provided 3D insights into the VS_2 nanoflower and nanotube structures. Electrochemical performance, evaluated through linear sweep voltammetry (LSV) and Tafel analysis, demonstrated that MoS_2 outperformed WS_2 and VS_2 , maintaining the catalytic activity order in both acidic and alkaline conditions. Electrochemical impedance spectroscopy (EIS) was employed to evaluate charge transfer resistance (R_{ct}), with MoS_2 nanostructures displaying the smallest R_{ct} . Surface area analysis indicated that MoS_2 nanotubes had the highest electrochemically active surface area (ECSA), attributed to strain and defect-rich surfaces. DFT calculations provided insights into the thermodynamic stability of nanotubes and nanoribbons, with VS_2 nanotubes exhibiting a lower energy of bending than MoS_2 and WS_2 . Additionally, DFT calculations on hydrogen adsorption free energy (ΔG_H) suggested that VS_2 basal planes have potential catalytic activity, contrary to experimental observations.

Conclusions

In summary, this study presents a comprehensive investigation of various transition metal dichalcogenides (TMD) nanostructures for HER activity. MoS_2 demonstrated superior performance, and despite its metallic-like nature, VS_2 exhibited lower activity. The combination of experimental and theoretical approaches sheds light on the factors

influencing TMD catalysis, emphasizing the importance of morphology, defects, and strain in designing efficient electrocatalysts.

Graphic:



Keywords:

2D, Electrochemistry, Electron Tomography, nanotubes