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Topic : Investigation of the Catalytic Role of Nanostructured Surfaces

Findings

The escalating global energy crisis, intensified by rising demand and the harmful impacts of burning fossil fuels, underscores the urgent need for sustainable energy solutions. Among alternatives, hydrogen stands out as a promising clean fuel due to its high energy density and clean emissions. However, the efficiency of hydrogen production, particularly through the water splitting, is intrinsically linked to the performance of the electrocatalysts employed. At present expansive Pt group metals (Pt, Pd, Ir) are the catalyst of choice due to their optimal performance. However, substitution of the expansive Pt group metals with earth abundant materials is the need of the hour to enable the scale of electrocatalytic hydrogen production within economical constraints. This PhD work delves into the potential of 2D materials, especially transition metal carbide (MXenes) and dichalcogenides (TMDs), as efficient catalysts for the hydrogen evolution reaction (HER).

In our initial study, we computationally examined the HER activity of Ti_2CO_2, a 2D transition metal carbide MXene decorated with Cu_3 and Cu_5 copper clusters. Density functional theory calculations showed that the Ti_2CO_2-Cu_3 catalyst outperformed pure MXene and Ti_2CO_2-Cu_5 in HER. Remarkably, the optimal ΔG^* of -0.08 eV on Ti_2CO_2-Cu_3 approached the activity of platinum, suggesting its potential as a cost-effective and efficient HER catalyst. Subsequently, we explored the HER activity of platinum and iridium-doped molybdenum carbide MXene (Mo_2CO_2). While the catalytic performance of Pt-doped Mo_2CO_2 was found to be inferior to that of pure platinum and Mo_2CO_2, the Ir-doped Mo_2CO_2 demonstrated significantly enhanced activity. Our calculation revealed that hydrogen adsorbed on hollow (centre) sites in Ir-Mo_2CO_2 has better catalytic activity compared with Mo_2CO_2 itself. This insight suggests that strategic doping of 2D materials, especially with iridium, can enhance the HER reaction, combining efficiency with economic viability.

In further exploration, we investigated the potential of copper nanoclusters to augment the performance of the HER in the MoS_2 basal plane. Our computational analyses underscored the pivotal role of cluster size, revealing that isolated Cu adatoms exhibit overly strong hydrogen binding, potentially impeding kinetics. Interestingly, our investigation demonstrated that Cu_3 clusters achieved a desirable, moderate binding energy of -0.15 eV, close to that of Pt catalysts. This meticulous assessment positions

precisely engineered Cu_3 nanoclusters as highly promising co-catalysts, unlocking abundant catalytic sites across MoS_2 through selective binding. By enhancing activity with earth-abundant materials, our strategic design represents a step towards economically viable and sustainable alternatives for hydrogen evolution.

On the experimental front, we synthesised layered molybdenum disulfide (MoS_2) nanostructures with a flower-like morphology on carbon substrate via a hydrothermal method using sodium molybdate and L-cysteine. X-ray diffraction, Fourier transform infrared spectroscopy, Scanning electron microscopy, and Raman spectroscopy confirmed the formation of 2H-MoS_2 and provided insights into the material's morphology and elemental composition.

Our theoretical and experimental studies underscore the potential of tailored 2D nanomaterials, like MXenes and TMDs, as efficient electrocatalysts for hydrogen production. The findings revealed that optimal HER kinetics can be achieved through strategic compositional engineering, including metallic dopants and co-catalysts. These catalysts could offer economical solutions to meet growing energy demands while addressing environmental challenges. Further refinements in nanoarchitecturing and surface functionalisation represent promising pathways forward.