Chapter 6

Summary and Future Scope

Summary

The extensive dependence on fossil fuels has numerous negative impacts on our environment due to their widespread utilization in various sectors to facilitate modern society. There is an urgent need for transition to sustainable energy sources that has the potential to meet the rapid increment in demand and hinder the adverse effects such as climate change and global warming. There are many renewable energy sources available that harness the consistent and natural energy flows present in our immediate environment. They encompass various forms, including bioenergy, direct solar power, geothermal energy, hydropower, wind energy, and ocean energy. To advocate the sustainable energy sources, H_2 is one of the best alternatives if its production is based entirely on renewable energy carriers. One of the techniques to produce H_2 in a green way is electrochemical water-splitting. Within the context of electrochemical water-splitting, this process can be divided into two key half-reactions: the HER and the OER. The HER involves the reduction half-reaction, while the OER pertains to the oxidation half-reaction. In both of these processes, the catalyst plays a pivotal role in reducing overpotential, thereby enhancing the efficiency of hydrogen production. So far, noble metals like Pt and others have proven to be the most efficient catalysts. Nonetheless, their rarity and costly procurement have posed significant obstacles to their widespread adoption. This urges the need of a catalyst that can overcome the drawbacks of these noble metals. Present thesis is based on the search of earth-abundant, cheap catalysts that are viable for this process of clean H_2 production. This thesis showcases a comprehensive study of various metal chalcogenides, employing DFT simulations to assess their potential as catalysts.

The first-principles based DFT formalism used to examine the ground state characteristics of the 2D systems under consideration are covered in **Chapter 2**. Starting with the traditional Born-Oppenheimer method, the newest developments in the fundamental DFT are discussed before moving on to the Kohn-Sham density-based approximations that serve as the basis of DFT. Using the plane-wave basis sets and pseudopotential theory. The long-range van der Waals dispersion correction, which was implemented on the QUANTUM ESPRESSO simulation programme, is discussed. A detailed investigation into the structural, electronic, optical, and catalytic properties of different metal chalcogenides has been conducted using DFT. This approach aims to gain an atomic-level comprehension of the catalytic mechanisms involved. Innovative and pragmatic methods have been employed to create new metal chalcogenide materials and regulate their catalytic capabilities.

Chapter 3, discusses a comprehensive analysis of the structural and electronic properties of pristine and alkali metal-doped $SnSe_2$ monolayers using first-principles based DFT simulations. Our investigation of the DOS has revealed that the pristine $SnSe_2$ monolayer exhibits semiconductor behaviour, while the incorporation of alkali metal dopants transforms these semiconducting monolayers into metallic materials. Furthermore, we conducted a site-dependent study of hydrogen adsorption to understand variations in adsorption capacities across different sites within the $SnSe_2$ monolayers. We observed that for both pristine and Na-doped $SnSe_2$ monolayers, the edge sites are the most favourable for hydrogen adsorption. In contrast, for Ca and K-doped $SnSe_2$ monolayers, the basal plane exhibits significant activity. Regarding oxygen adsorption, the basal plane is found to be the most preferential site for both pristine and doped $SnSe_2$ monolayers. Moreover, the Gibbs free energy analysis of these materials suggests their potential suitability as catalysts for either HER or OER. Our results indicate that the Na-doped $SnSe_2$ monolayer is particularly well-suited for HER catalysis, as the Gibbs free energy approaches to ideal value. Meanwhile, the Ca-doped $SnSe_2$ monolayer emerges as a promising candidate for OER catalysis, followed by the Na-doped and pristine $SnSe_2$ monolayers. In summary, our findings suggest that the overall catalytic activity of the $SnSe_2$ monolayer can be significantly enhanced with the introduction of alkali metal dopants.

In **Chapter 4**, we delved into the structural and electronic characteristics of both pristine and defective $SnSe_2$ monolayers, focusing on their HER activity. To assess the catalytic potential of these materials, we calculated $\Delta E_{ads}^{H}$and ΔG^{H} for hydrogen adsorption. In the case of pristine $SnSe_2$, we observed that the ΔG^{H} values fell considerably short of what is ideal, indicating a lack of reactivity towards HER. To enhance the catalytic efficiency, we introduced various defects into these materials, which had a significant impact on their electronic properties. Specifically, for the V_{Se} defect, hollow site adsorption yielded a satisfactory ΔG^{H} value of 0.40 eV, while the Sn and Se sites showed values of 0.54 eV and 0.48 eV, respectively. In the case of the V_{Se_2} defect, ΔG^{H} values indicated that the Se site was more favourable for catalysis compared to the Sn site and the hollow site. When considering the V_{SnSe_3} defect, both Se sites and hollow sites exhibited favourable ΔG^{H} values of 0.27 eV, -0.22 eV, and 0.19 eV, respectively. Lastly, with the V_{SnSe_6} defect, the catalytic efficiency for H adsorption at the hollow site surpassed that at the Sn site. Among all the defects studied, it became evident that the V_{SnSe_3} hollow site was the most promising candidate for HER, followed by the V_{SnSe_3} and V_{SnSe_6} Se sites and hollow sites, respectively. In general, defects had a significant impact on modulating the HER performance of the $SnSe_2$ monolayer, approaching ideal values in certain cases. We hope that our predictions based on DFT will inspire experimentalists to design efficient HER catalysts based on $SnSe_2$.

In **Chapter 5**, we conducted an in-depth examination of the structural and electronic characteristics of pristine and defected HfS_2, $HfSe_2$, and Janus HfSSe, focusing on their potential as catalysts for the HER. Our calculations revealed that HfS_2 and HfSSe exhibited electronic band gaps of 1.56 eV and 1.04 eV, respectively, making them appealing candidates for use as photocatalysts. In contrast, $HfSe_2$ had a narrower band gap of 0.68 eV, suggesting its suitability as an electrocatalyst. To assess their catalytic capabilities, we calculated $\Delta E_{ads}^{H}$and ΔG^{H} for hydrogen. Our findings of the Janus HfSSe are in accordance with the previously studied Janus SeMoS, that displayed promising catalytic performance for HER. The order of hydrogen adsorption efficiency is as follows: HfSSe > HfS_2 > $HfSe_2$. To further enhance their catalytic efficiency, we introduced various defects into these materials, which significantly affected their electronic properties. For HfS_2, the presence of a vacancy (V_{Hf}) resulted in a lower ΔG^H compared to the presence of a vacancy (V_S) or the pristine structure. Similarly, in $HfSe_2$, V_{Hf} exhibited lower ΔG^H values compared to V_{Se} or the pristine structure. In the case of Janus HfSSe, V_{Hf} displayed the lowest ΔG^H, followed by V_{Se} and V_S. Our analysis suggested that defected HfS_2 exhibited the most favourable ΔG^H, followed by defected $HfSe_2$ and defected Janus HfSSe, with values of 0.03 eV, 0.21 eV, and 0.25 eV, respectively. These observations lead us to the conclusion that V_{Hf} in HfS_2 is particularly well-suited for HER, as its value approaches the ideal value. In summary, our study highlights the significant role of defects in enhancing the catalytic activity of TMDs.

Future scope

Our primary objective must be the development of a highly efficient catalyst for green energy production. While there have been some noteworthy advancements in this field, there remains a significant scope for improvement. Recent trends in materials development for energy applications underscore the urgent need for an evolution in material design to optimize efficiency. DFT studies have emerged as a valuable tool for gaining insights into the various steps of chemical reactions. They enable us to explore different reaction pathways and address critical questions through theoretical approaches. This, in turn, aids in the development of superior catalysts that can enhance the overall effectiveness and selectivity of chemical processes. To transcend the knowledge gained from specific cases, there is a need to establish a universal theory that can encompass and provide explanations for all instances of metal catalysis. Achieving this goal necessitates collaborative efforts from both physicists and chemists, particularly those specializing in solid-state chemistry, surface physical chemistry, and chemical reactivity. In broad terms, future research directions can be outlined as follows:

1. Innovate and formulate new concepts in catalyst design to enhance the adsorption and activation of reactants while ensuring phase stability and a high density of catalytically active sites.
2. Utilize microkinetic modeling to gain insights into extreme environmental conditions such as variations in pressure and temperature, as well as under defective conditions.
3. Prioritize the development of theoretical characterization techniques capable of mapping transient chemical changes with improved spatial resolution.
4. Design and create economically feasible, environmentally friendly, and scientifically ideal catalysts.

My future endeavours aim to bridge the gap between my current knowledge of methods for studying material properties and my future contributions to materials science. This will involve the integration of existing and advanced theoretical techniques with relevant computational tools to advance the field.