A Density Functional Theory Investigation on Hydrogen and Oxygen evolution reaction of Metal Chalcogenides

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ABSTRACT

Hydrogen possesses the potential to become an excellent energy carrier for a sustainable energy economy due to high energy density and ecologically benign characteristics to appease the increasing energy demand. Hydrogen production from water via electrocatalysis is widely investigated these days with several electrocatalysts in order to make it economically viable. The discovery of graphene has led to an intensive research interest in two-dimensional (2D) materials. Owing to the lack of an electronic band gap of graphene, the research for novel materials with semiconducting nature has increased tremendously. Of all the materials that have been reported, the unique layered 2D transition- metal dichalcogenides (2D TMD's) have attracted humongous attention because of their excellent electrocatalytic activity towards the cathodic half-cell reaction of water electrolysis, the hydrogen evolution reaction (HER). The major drawback of these materials is their inactive basal plane as compared to their edge sites.

In this Ph.D. dissertation, we have systematically studied the fundamental properties and catalytic activity of Tin-diselenide ($SnSe_2$ and Hafnium based chalcogenides) to observe the variation in its electrocatalytic efficiency through hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) by introducing dopant or defect. The state-of-art density functional theory (DFT) based computations are performed for estimating the catalytic activity of the pristine and doped $SnSe_2$ by means of evaluating the adsorption and Gibb's free energies subjected to hydrogen and oxygen adsorption. As far as the catalytic activity of $SnSe_2$ with dopants is concerned, the Na-doped $SnSe_2$ among all shows the best catalytic performance over its edge site; whereas K and Ca doped $SnSe_2$ show basal plane as preferred catalytic site. The structural, electronic and catalytic properties of hafnium diselenide

($HfSe_2$), hafnium disulphide (HfS_2) and janus HfSSe layered structure are studied. Further, defects at various sites of these structures are created to observe the alteration in the properties. The study is enhanced by employing an in-depth explanation of both Tafel and Heyrovsky’s reactions. An amendatory band-center model is developed to interpret the defect-dependent HER activity in these structures. Finally, the study of $SnSe_2$ is done by employing various point defects and the changes in the catalytic activity is noted.

CONTENTS

INTRODUCTION

As global warming issue urges to quite the use of fossil fuel as source of energy to overcome demand we need a sustainable energy system that is eco-friendly and fulfill the demand of growing population. One of the cleanest energy suppliers is hydrogen molecule itself. The discovery of graphene and other two-dimensional (2D) materials with exfoliation techniques have set the foundations for the manufacturing of single layered sheets from any layered 3D material [1, 2]. Each layered material, when thinned to its physical limits, exhibits novel property different from its bulk counterpart [3,4]. However, the true potential of these materials is realized recently for advanced technological applications due to excellent optical, electronic and mechanical properties [5-10]. After huge application of graphene, researchers are keen to develop other layered 2D materials which can accomplish the requirements analogous to graphene and also overcome limitations of graphene, that is zero band gap, oxidative nature and many more [11-13]. It was shown by Frindt et al. [14] that layered van der Waals materials such as metal chalcogenides, could be mechanically and chemically exfoliated into few and single layers. These layered metal chalcogenides such as, MoS_2, WS_2, Janus WSSe and many more have been identified as semiconducting 2D layered materials. Furthermore, transition metal chalcogenides possess MX (M: Mo, W, V..; X: S, Se and Te) type stoichiometry; whereas transition metal dichalcogenides possess MX_2 type of stoichiometry. In case of MX_2, M is a transition metal which is sandwiched between the two layers of chalcogenides atoms. Layered 2D nanostructures with atomic scale thicknesses may exhibit peculiar and fascinating properties in contrast with those of their bulk parent compounds. Both the experimental and theoretical results show that the 2D semiconductors have exceptional properties that can result in novel and important breakthroughs in the field of nanomaterials and nanodevices [7-9]. As these structures have distinctive properties, they can be utilized for various cutting-edge technological fields, such as solar cells, energy storage devices, electro-catalysts, photo-catalysts, bio-sensors, MOSFETS and CMOS etc [14, 15-17].

Metal chalcogenides make its own place among all other 2D materials due to its versatility and unique properties such as electro catalyst, photo-catalyst for production of H_2 via water splitting mechanism, reduction of CO_2 and energy storage that has attracted scientist and researchers [15-17]. The literature study reveals that the electro-catalysts studied till date are based on expensive metals like Au, Pt, Pd, Ru [18-20] which are costly and availability is also limited whereas metal chalcogenides are non-precious and abundant. There are many methods to produce hydrogen. Among them, the electrochemical splitting of water has attracted a lot attention and is robustly effective method to produce carbon free source of hydrogen [21–23]. Moreover, the water splitting method is consists of two half reactions: the evolution of H_2 that is $2H+ + 2e- \rightarrow H_2$ and evolution of O_2 that is $2H_2O \rightarrow 4H+ + 4e- + O$. Moreover, one of major drawback of the metal chalcogenides is that its edges are more reactive sites as compared to basal plane that become one of the hindrance for production of hydrogen [21]. To overcome these, basically one needs to increase the ratio of edges to basal plane in these materials. Moreover, metal selenides are promising candidates for electrocatalyst due to low cost fabrication and shows higher electrocatalytic activity [21]. Further, it is shown that doping can improves the hydrogen evolution reduction at its basal pane [22-27]. Moreover, it is interesting to note that the HER activity is more in metallic electro-catalyst as compare to semiconductor electro-catalyst [21]. The electronic properties of materials can be tuned by applying strain, electric field, doping and defect which will enhance the HER and OER activity of materials [22-27]. Moreover, experimentally also it is shown that dopant enhanced HER electro-catalytic activity as compare to pristine [27]. In short, the inevitable need of renewable energy and storage with batteries, hydrogen as well as fuel cells are considered for potential applications. The evolution of metal chalcogenides show a path to replace expensive noble metals as electro-catalysts and they can be used for highly efficient solar energy conversion devices as their catalytic performance has much lower cost [26] environmental compatibility with carbon-free energy source. In the present work, we mainly focus on the study of structural, electronic and catalytic properties of metal chalcogenides. Thereafter, we enhance their properties by doping dopant and creating vacancy which helps to understand mechanism to have good catalyst for water splitting mechanism. We have studied two class of 2D transition metal chalcogenides such as tin diselenide ($SnSe_2$) and hafnium chalcogenide family which is hafnium diselenide ($HfSe_2$), hafnium disulphide (HfS_2) and it's janus structure HfSSe monolayered structure using density-functional theory. We tuned their properties for better applications as hydrogen production and can be used for other applications such as hydrogen storage and solar cell which is out of scope for present work but will be considered as future scope work.

OBJECTIVES

The aim of this proposed work is to investigate the structural, electronic and optical properties of various metal chalcogenides. Our aim will provide the better understanding of physical and chemical properties of metal chalcogenides and detailed study of doping induced characteristic of metal chalcogenides. The main focus of this work is to investigate the effect of doping on electronic and optical properties to analyze the change in catalytic effect of materials. Our aim is to provide the understanding of enhancement of catalytic effect before and after tuning properties of metal chalcogenides. However, the specific objectives of the present work are following:

1. First the determination of ground state and geometry structure of metal chalcogenides using density functional theory.

2. To investigate the possible electronic properties of metals chalcogenides and modification electronic properties of metal chalcogenides for surface phenomena via charge transfer induced that is by doping dopant, applying strain or by creating defect.

3. To study the interaction and stabilization of the metal chalcogenides at specific sites with foreign atoms and gases such as hydrogen and oxygen.

4. The calculation of work function to understand surface phenomena that is interaction between adsorbate (metal chalcogenides) and adsorbent (hydrogen or oxygen atoms). As the change in work function is related to presence of minute amount of contamination on a monolayer or occurrence of surface reaction

5. The calculation of optical properties of given metal chalcogenides helps us to know potential applications of these materials such as photo catalyst or electro-photo-catalyst for hydrogen evolution reaction.

SUMMARY OF THE RESEARCH WORK

The present thesis is organized in the following manner:

Chapter 1 is about the progress and development of two-dimensional (2D) materials for their unique properties and their applications in the novel fields such as electronics, optical, hydrogen storage, nanocatalysis for hydrogen evolution reaction (HER) and solar cells applications. Further, the prediction of new 2D materials provides an emerging way to have better technology and applications to society. Today’s world not only demands better technology for their comfort but also required energy for electronic appliances. Therefore, there is a need of eco-friendly production of renewable sources. One of the cleanest forms of energy is hydrogen which is produced by the process called water splitting. Moreover, many 2D materials such as TMD, borophene, graphene have attracted a lot attention as a catalyst for hydrogen evolution reaction to have cost effective catalyst as compared to platinum. Further, studies shows that the catalytic activity of these classes of 2D materials can be enhanced with doping, creating defect, applying field and strain and including substrate. Newly predicted 2D materials are also equally potential as compared to existing 2D materials as their bands nature varies from semiconductor to metallic. The structure of tin diselenide is honeycomb structure similar to those of MoS_2, SnS_2 etc. Besides, it overcomes the drawback of TMD's having active edge sites leaving basal plane inactive by tuning of properties mentioned by above techniques. This shows the importance of studying and the need of tuning properties of aforementioned materials for potential applications.

Theoretical description of computational methodology used throughout the work is presented in **Chapter 2**. In this chapter, theoretical concepts which are the basis of density functional theory (DFT) are presented and discussed. In particular, all quantities which help to calculate the electronic, dynamical and catalytic properties of 2D materials on the basis of DFT are discussed. We present all basic ideas of many body problems, Born-Oppenheimer, Hartree and Hartree-Fock approximations followed by density based method and Kohn-Sham equation in chapter 2. Moreover, the use of plane wave to represent electron wave functions and density needed to deal with valance and core electrons implemented in Quantum Espresso simulation code are discussed. We also discuss the Grimme's dispersion correction which is important not only to predict correct cohesive and adsorption energies but also important to consider van der Waals interaction which is important for layered systems.

In **Chapter 3,** we have reported the results of our systematically investigated, stability and electronic properties of two-dimensional honeycomb structure of tin diselenide ($SnSe_2$) and studied its catalytic activity for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) using density-functional theory (DFT) based first-principles calculations. We have included dispersion correction (DFT-D2) to get accurate adsorption energy to have better understanding of hydrogen and oxygen adsorption on $SnSe_2$ for HER and OER. From our calculations, we found that the $SnSe_2$ has indirect band gap of 0.80 eV and shows potential for HER as photocatalyst. Furthermore, we sieved the dopant for better catalytic activity through ban gap modulation as band gap is one of the important parameters for catalytic activity. The fundamental band gap of $SnSe_2$ can be altered with functionalization of $SnSe_2$ by alkali metal dopants Na (Sodium), K (Potassium) and Ca (Calcium). We found that on doping of Na, K and Ca dopants the semiconducting nature of pristine $SnSe_2$ becomes metallic in nature. The Gibb's free energy for pristine and Na, K and Ca doped systems for hydrogen adsorption is 0.79 eV, -0.29 eV, -1.29 eV and 0.72 eV respectively. Also, the Gibb's free energy for pristine and Na, K and Ca doped systems for oxygen adsorption is -0.69 eV, -0.54 eV, -1.72 eV and -0.45 eV respectively. Our results show that the Na-doped $SnSe_2$ monolayer is more suited for HER catalyst as the Gibb's free energy is close to zero. The Ca-doped $SnSe_2$ monolayer is the better candidate for OER catalyst, followed by Na-doped and pristine $SnSe_2$ monolayers.

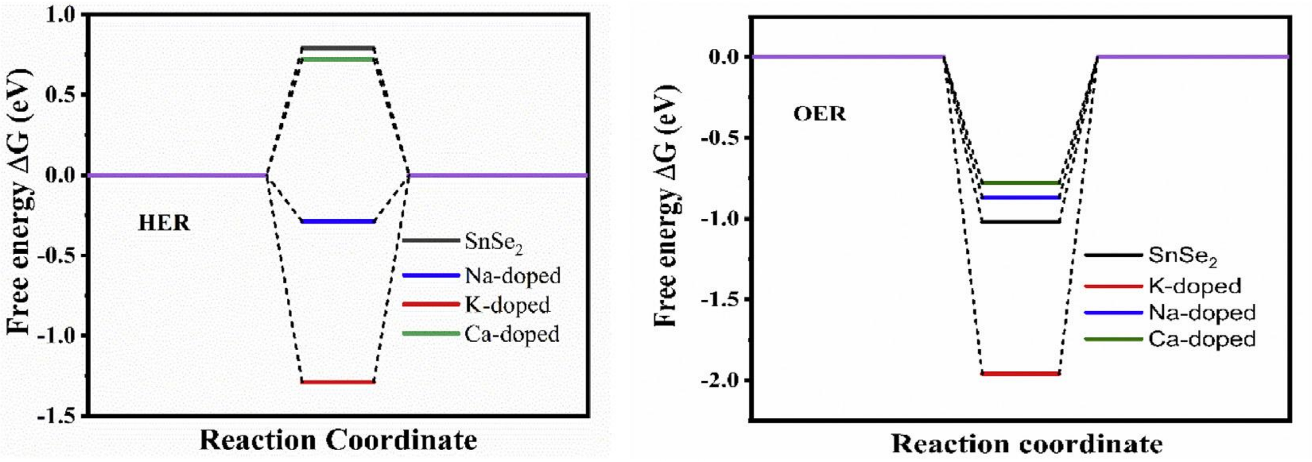

Fig (1). Reaction coordinate (a) HER and (b) OER of pristine SnSe2 and doped-SnSe2

In **Chapter 4**, we reported the results of our systematically investigated, stability and electronic properties of the two-dimensional hafnium-based transition metal chalcogenide (HfX; X=S_2, SSe, Se_2) that is HfS_2, HfSSe (Janus), and $HfSe_2$ monolayers. We investigated its catalytic activity for the hydrogen evolution reaction (HER) using density functional theory (DFT). For a better understanding of hydrogen adsorption on HfX for HER, we have applied dispersion correction (DFT-D2) to obtain accurate adsorption energy. From our calculations, we found that the band gap of HfS2, HfSSe, and $HfSe_2$ is 1.28 eV, 0.98 eV and 0.68 eV respectively. Thereafter, we calculated the Volmer Gibbs free energy at two different sites namely the basal plane (on the top of Hf atom) and edge site (near to corresponding chalcogenide site), we observed that the basal plane was indeed inactive in the case all three structures. Moreover, we found that the S-edge site is more active than Se site and follows the Gibbs free energy sequence HfSSe (1.40 eV) > HfS_2 (1.62 eV) > $HfSe_2$ (1.67 eV). The band gap of HfS_2 and HfSSe (~1eV) are in the visible region and can be utilized as a photocatalyst for HER. The Jannus monolayer exhibit superior catalytic activity compared to its parent counterpart (HfS_2 and $HfSe_2$ monolayer). Previously, defect engineering of MoS_2 is shown to be an effective tool for enhancing the basal activity of the MoS_2 monolayer. Therefore, we have studied two mono defects of hafnium and sulphur/selenide for better catalytic activity through band gap modulation. We found that Hf defect leads to the lower Volmer Gibbs free energy compared to the S/Se defect in HfS_2, HfSSe and $HfSe_2$ monolayer. The lowest Volmer Gibbs free energy is at the Hollow site (0.22 eV) for the Hf-defect $HfSe_2$ monolayer, S-edge site (0.25 eV) for the HF-defected Janus monolayer and Hf site (0.03 eV) for Hf defected HfS_2 monolayer. We observed that basal plane activity enhances for Hf defect HfS_2 monolayer, defect engineering is quite a powerful method for enhancement of it. Thereafter, we analyzed the Volmer-Tafel and Volmer-Heyrovsky mechanisms to have dominated mechanisms for hydrogen production with the lowest achieved Volmer Gibbs free energy cases. We observed Volmer-Heyrovsky is dominated by Volmer-Tafel reaction, Hf-defect HfSSe and HfS2 monolayer are best candidate for the Hydrogen Evolution reaction.

In **Chapter 5**, we have analyzed the effect of different defects on the catalytic properties of tin diselenide($SnSe_2$). We investigated its catalytic activity for the hydrogen evolution reaction (HER) using density functional theory (DFT). For a better understanding of hydrogen adsorption on $SnSe_2$ for HER, we have applied dispersion correction (DFT-D3) to obtain accurate adsorption energy. From our calculations we observed that, creating defects on various sites indeed improves the catalytic efficiency. We have created 9 types of point defects in the system. They are: monoselenide vacancy (V_{Se}), diselenide vacancy (V_{Se2}), vacancy complex of Sn and nearby three selenium (V_{SnSe3}), vacancy complex of Sn and nearby three diselenide pairs (V_{SnSe6}), antisite defects where a Sn atom substituting a Se atom (Sn_{Se}), a Sn atom substituting a Se_2 atom (Sn_{Se2}), a Sn_2 column substituting a Se_2 column (Sn_{2Se2}), a Se atom substituting a Sn atom (Se_{Sn}), Se_2 column substituting a Sn atom (Se_{2Sn}). Among all the defects created the below four structures give stable configuration for further catalytic study. They are diselenide vacancy (V_{Se2}), vacancy complex of Sn and nearby three diselenide pairs (V_{SnSe6}), a Sn_2 column substituting a Se_2 column (Sn_{2Se2}) and a Se atom substituting a Sn atom (Se_{Sn}). All the possible adsorption positions for a single H atom are considered and the most stable configuration for V_{Se2} is the location at Se vacancy, for V_{SnSe6} the H atom prefers to adsorb on the bridge site of two Sn atoms, for Sn_{2Se2} the H atom favours to bond with Sn atom instead of Se atom and for Se_{Sn} the H atom tends to bond with the Se atom with dangling bonds. The Gibb's free energy calculated gives us the insight of the catalytic efficiency. The obtained Gibb's free energy for pristine $SnSe_2$ is 0.79 eV (~ 0.80 eV). The obtained Gibb's free energy of Volmer reaction for different adsorption sites of defects V_{Se2} is 1.72 eV and 0.46 eV, V_{SnSe6} is 0.967 eV and 0.359 eV and for Se_{Sn} is 0.85 eV. The defects V_{Se2} and V_{SnSe6} gives us the energy lower than the pristine system. Further, we study the Tafel and Heyrovsky reactions. The d band model study is also incorporated for further detailed study.

The overall investigation of our results on structural, electronic and catalytic properties of 2D metal chalcogenides using DFT has been summarized in **Chapter 6**. The results show the pathway of engineering the properties of the system by means of engineering with the dopants and vacancies. Finally, we provide a brief overview of the potential areas for future research to conclude our thesis.

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