

Chapter 1 Introduction and Literature Survey

1.1 Introduction

The world mostly uses nonrenewable fossil fuels to generate a large amount of electricity and heat energy for use in numerous daily activities. Although this energy helps people meet their basic human requirements, its production methods are in conflict with the capacity of the human race to continue to meet their requirements. It is significant to mention that burning fossil fuels causes environmental issues such as global warming, ozone depletion, ocean acidification, and resource depletion [2]. These issues have had a significant impact on the social and economic development of every country, as well as on human, plant, and animal life. The renewable energies (e.g., solar or wind energies) will play a vital role as it is well accepted and a powerful combatant to climate change because they emit little to no carbon dioxide and other greenhouse gas emissions in energy generation process. Green energy is a type of energy that often derives from renewable energy sources like sun, wind, geothermal, biomass, and hydroelectricity. As an example, for energy generation system, solar cells use photovoltaic (PV) panels to directly convert sunlight into power. Despite the fact that a lot of sunlight is received around the world each year depending on their geographic location, the relatively expensive cost of installing solar panels has limited the uses of this resource [3]. As another example, piezoelectric systems are used to convert mechanical/vibrational energy into electricity and vice-versa with zero carbon footprint. The stimuli for piezoelectric materials can be human walking, wind, rain, tide and wave etc. The major disadvantage of piezoelectric materials is that they are extremely brittle nature causes limitations and the devices have less than 10% efficiency [4]. Thus, finding solutions to reduce the development of cost effective and sustainable renewable energy technologies is need of the hour. The hydrogen energy offers a practical

answer with a host of benefits, including purity, availability, and environmental friendliness. Specifically, hydrogen fuel offers the highest energy density and is the most environmentally friendly fuel. As a result, sustainable hydrogen generation has drawn a lot of attention and become increasingly crucial for resolving the energy crisis and environmental problems. Hydrogen is produced by separating it from the hydrogen-containing compounds and primarily three types of hydrogen are available based on processing methods. Most of the hydrogen comes from steam methane reforming process, where methane reacts with high-temperature steam and catalyst to produce hydrogen, carbon monoxide, and carbon dioxide. This type of hydrogen is known as grey hydrogen. The other type i.e., blue hydrogen is produced from reaction of natural gas with hot steam and a catalyst. As a third type of hydrogen, green hydrogen is produced by renewable energy like solar, wind etc. Generally, green hydrogen is produced using electrolyzers, which splits water into hydrogen and oxygen using an electric current. This method is the most environmentally friendly method for producing hydrogen [5,6]. The produced hydrogen should be kept in high pressure vessel and can be used in fuel cell to transform the chemical reaction energy of an oxidising agent and hydrogen to supply electrical energy. The Pt catalyst possess superior catalytic activity towards hydrogen evolution reaction (HER) but the extensive use of the Pt group electrocatalysts may be limited due to their scarcity and high cost. As alternatives to the unique Pt catalyst for HER, non-precious metal alloys and metal-nonmetal based catalysts such as chalcogenides (MoS_2 , MoSe_2 etc.), phosphides (Ni_2P , Co_2P), carbides (Mo_2C , W_2C), and nitrides (phosphorus nitride, phosphorus nitride) are being investigated [7,8].

In case of energy storage, battery and supercapacitor are the most potent devices. An electrolyte reacts with metals in an electrochemical battery through redox reactions to generate large amount of electricity. However, batteries have certain disadvantages, such

as low power density, limited life cycle and comparatively slow response in the context of certain applications. Thus, the extensive use of batteries is explicitly limited in energy storage systems where high energy density is required. Electrolytic capacitor can be good alternative for delivering high power due to the charge storage via electrostatic field but suffers with very low energy density. The supercapacitors devices work as a bridge between the electrolytic capacitor and rechargeable batteries. The main functional difference between a battery cell and a supercapacitor is that although batteries are able to store more energy per unit mass, supercapacitors are able to store and discharge more short-term power. Supercapacitors have much higher capacitance values of a tenth of a Farad to several thousand Farads. Supercapacitors store energy directly as an electrostatic charge by the formation of a double layer in the electrode/electrolyte interphase [9,10]. Carbon nanostructures (activated carbon, nanotubes, graphene or reduced graphite oxide) transition metal oxides (RuO_2 , MnO_2 etc.), transition metal dichalcogenides (TMDCs like MoS_2 , MoSe_2 etc.) and conducting polymers (Polyaniline, polypyrrole etc.) have been investigated as supercapacitor electrode materials [11,12].

In the present thesis, we have investigated the HER activity and capacitive performance of reduced graphite oxides (rGO) and molybdenum disulfide (MoS_2) nanostructures among carbon and TMDCs nanostructures. In the following section, we will look in to the physical and chemical properties of rGO and MoS_2 nanostructures suitable for energy applications specifically for HER and supercapacitors.

1.2 Reduced Graphite Oxide

The discovery of atomically thin graphene from graphite in 2004 by Novoselov *et al.* has sparked a study into the fundamental properties and potential applications of two

dimensional (2D) materials owing to their unique physical and chemical properties [13,14]. The term "two-dimensional material" refers to a group that is weakly connected between layers by van der Waal forces. The 2D materials exhibit a variety of electrical characteristics such as indirect and direct band gaps in the ultraviolet, visible to infrared regions and can be metals, semimetals, insulators and semiconductors [15–17]. Among 2D materials, graphene has emerged as rising star in the field of materials science. Graphene inherently possess atomic-thin morphology, flexibility, high carrier mobility, huge surface area, good thermal conductivity and mechanical strength, which makes it good candidates for energy generation and storage applications [18,19]. Graphene is referred as the origin of all graphitic forms, including 3D stacked graphite, 1D rolled carbon nanotubes, and 0D buckyballs [20]. Among the broad application prospects in electronic devices, biological and chemical sensing applications, graphene-based materials are the most valued and researched for energy conversion and storage. There are two general methods to synthesize graphene: top-down and bottom-up approaches. The top-down method uses mechanical or liquid phase exfoliation to produce graphene materials by performing the breakdown of graphite. The weak van der Waal force between the layers, which enables the separation of individual 2D layers from their bulk equivalent, makes these exfoliation methods appropriate for the synthesis of 2D materials. The mechanical exfoliation is based on application of mechanical force using a scotch tape for peeling process of highly oriented pyrolytic graphite. The limited yield and tiny flake size are the principal drawbacks of this method. As a result, the graphene and other 2D materials synthesis via this process can be performed on basic laboratory level only. Although there have been substantial breakthroughs, but it is still extremely difficult to produce inexpensive, high-quality graphene on an industrial scale.

On the other hand, the bottom-up technique uses epitaxial growth, chemical vapour deposition (CVD) and physical vapor deposition (PVD) methods. These are more restricted to specialised metallic substrates where high quality, but sparsely produced, graphene is created. They also require expensive equipment, synthesis at high temperatures, and are time-consuming [21–23]. The epitaxial growth technique for graphene synthesis on silicon carbide requires high temperature ($> 1100\text{ }^{\circ}\text{C}$) for sublimation of silicon and the remnant carbon is restructured to create graphene at these temperatures [23]. The CVD is distinctive technique to synthesize the graphene via pyrolysis of hydrocarbon compounds on metal catalyst surface at higher under low or ultrahigh vacuum condition [24]. In general, bottom-up methods are tedious, expensive with low production efficiency, which limits their usefulness in large scale industrial applications. Among all techniques, chemical exfoliation method is significant and popular top-down process for the synthesis of few-layer graphene nanostructures. In this technique, the bulk materials are exfoliated using a variety of mechanical procedures such as direct exfoliation of graphite using sonication, electrochemical reduction, shearing, stirring, grinding, and bubbling, where common organic solvents and/or functionalization are also used [25–27]. One of the finest methods for synthesizing few layer graphene is chemical reduction of graphite oxide (GO), which is an oxygen intercalated graphite structure. In 1958 William S. Hummers and Richard E. Offeman established a successful and extensively used method for chemical oxidation of graphite to form GO [28–30]. In this process, initially interlayer distance between graphite sheet is increased via intercalation of different oxygen containing groups. Upon heating in vacuum/inert atmosphere, the strong repulsion of oxygenated groups takes place and graphite sheets are exfoliated into few layer graphene or also named as reduced graphite oxide (rGO). The general structures of rGO is given in **Figure 1.1**. The cost effective rGO possess features similar to those of graphene, such as reasonably strong conductivity, good

surface area etc. In another method, reducing agent is used to remove the most oxygenated groups possible to produce few layer graphene or rGO. Since the reduction of GO regulates all the physicochemical properties of rGO, the inclusion of an efficient reducing agent is essential. Numerous reducing agents are used for the effective reduction of GO, including hydrazine (N_2H_4), sodium borohydride ($NaBH_4$), ascorbic acid, hydroiodic acid (HI), amino acids, plant extracts, etc. However, the reduction mechanism are not clearly known [26], [31–33]. However, irreversible agglomeration in chemical exfoliation prevents further processing and use. Therefore, studies have concentrated on finding ways of preventing agglomeration of graphene sheets.

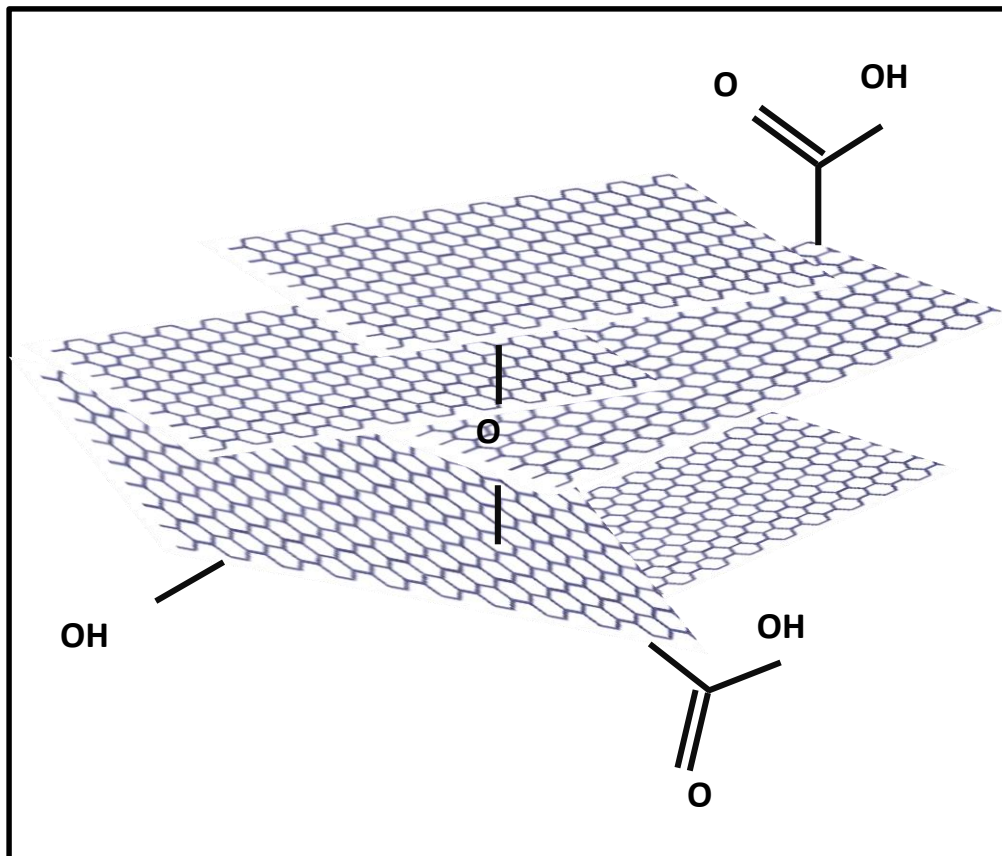


Figure 1.1 Schematic of few layer reduced graphite oxide.

1.2.1 Properties of Reduced Graphite Oxide

Electrical Property

The electrical property of graphene, consisting of 2D layers of one atom thick sp^2 carbon, is closely related to its π bond. It is an electrically conductive material with high electron mobility ($25 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$) and electrical conductivity (6500 S m^{-1}). In response to the necessity of rGO for commercial applications, researchers have been looking into several methods to enhance the production of electrically conducting rGO via choosing appropriate reduction methods for GO. Stankovich *et al.* utilized colloidal suspension of GO and reduced it using hydrazine hydrate [34]. The resultant product shows conductivity of $2 \times 10^2 \text{ S m}^{-1}$ which is higher in five order of magnitude than conductivity of GO. Voiry *et al.* utilized a conventional microwave oriented reduction (at 1000 W for 1–2 sec) technique to form rGO nanosheets, which improved the electron mobility $\sim 0.1 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ in field effect transistors [35]. These higher conducting of rGO is promising candidate for electrode materials in supercapacitor applications.

Thermal Property

Strong in-plane carbon bonding in 2D graphene leads to the high thermal response of graphene. Thermal conductivity is detrimental by the presence of defects, edge scattering and doping. The rGO also show high thermal conductivity due to the high aspect ratio and extensive interfacial contact area of rGOs, which provides a path of lower thermal to phonons. Additionally, high orientation and large sheet size of rGO restrict thermal transfer along borders [36]. Renteria *et al.* [37] showed the improved in-plane thermal conductivity of rGO ($\sim 61 \text{ W m}^{-1} \text{ K}^{-1}$) prepared via thermal annealing of GO at higher temperature of $1000 \text{ }^\circ\text{C}$. Similarly, Zeng *et al.* showed the improvement in thermal conductivity of rGO

($\sim 118 \text{ W m}^{-1} \text{ K}^{-1}$) with increasing annealing temperature (1000 to 3000 K) and utilized it for thermal sensors [38].

Mechanical Properties

This property mainly involves Young's modulus and fracture strength. Graphene is the strongest ever known material (200 times that of steel) with 130 GPa of tensile strength. It is also very light material weighing about 0.77 mg m^{-2} with Young's modulus to be $1.0 \pm 0.1 \text{ TPa}$ (thickness assumed is 0.335 nm). Graphene is a promising contender because of this exceptional feature for applications in nanoelectromechanical systems or other flexible devices. The rGO nanostructures shows lower Young's modulus compared to graphene due to the presence of number of surface groups and defects left over from oxidation or other treatment operations. Gomez *et al.* synthesized monolayer rGO via thermal annealing of GO in a hydrogen environment and obtained Young's modulus of $250 \pm 150 \text{ TPa}$ [39].

Optical property

Growing world demands for a flexible transparent electrode for applications in touch panels, flexible displays, solar cells, thin film photovoltaics, etc. The photonic device applications of graphene are of particular interest due to its most intriguing and crucially controllable optical characteristics. The rGO has several particularly intriguing applications in heterojunction photovoltaic systems as replacement for indium tin oxide (ITO) due to the dearth of costly indium, and other unfavourable properties [40, 41]. The superior flexibility of rGO films over ITO, provides an additional benefit for device application. Yin

et al. synthesized rGO films via thermal reduction of GO showing optical transmittance~65% and utilised it in photovoltaic devices [42].

Chemical property

The rGO nanosheets are commonly modified with oxygen and nitrogen containing functional groups, which provide it higher degree of wettability and conductivity. It has highest ratio of edgy carbon and dangling bonds in comparison to other carbon nanostructures like nanotubes, buckyballs. The curved and wrinkled surface with carbon atom at the edges provide high defect and enhanced electrochemical activity to rGO nanosheets. High surface area, microporosity, conductivity and availability of oxygen containing functional group of rGO sample makes it a potent candidate for variety of electrochemical applications. The rGO shows high degree of stability in both acidic and basic medium, which makes it suitable candidate for use as electrode in variety of electrochemical devices.

1.3 Molybdenum Disulfide (MoS₂)

The MoS₂ is class of 2D layered transition metal dichalcogenides (TMDCs) that feature the chemical formula MX₂, where M stands for the transition metal element (Mo, W etc.) and X represents chalcogen elements (S, Se, Te etc.). The layers of bulk MoS₂ structure are coupled with van der Waals forces similar to graphite, while the intra-layer Mo-S bonds are covalent in nature [43,44]. The van der Waal force is several orders of magnitude weaker than the in-plane covalent bonding. In monolayer MoS₂, Mo (+4) and S (-2) are arranged in S-Mo-S orientation and in each layer one Mo atom surrounding by six S atoms. Based on atomic arrangement of Mo and S atoms, MoS₂ can exist in three different phases- 1T, 2H, and 3R, where the digit (1, 2 and 3) denotes the number of layers within a single crystallographic unit cell, and the letter denotes the crystallographic

symmetry (T-trigonal, H-hexagonal, and R-Rhombohedral), as shown in **Figure 1.2**. Among these three polymorphs of MoS₂, 2H is the most stable and abundant polytype in earth's crust, while the unstable 3R phase is observed in chemically synthesized MoS₂ and has a rhombohedral symmetry with three layers per unit cell. In 2H and 3R phase Mo atom is prismatically coordinated to six surrounding S atoms. However, the 1T phase is formed due to the disorientation of one of the sulfur layers in MoS₂ and it possesses higher energy and thus less commonly found in the natural form. In 1T phase, the Mo atom is anti-prismatically coordinated to six surrounding S atoms [45–47].

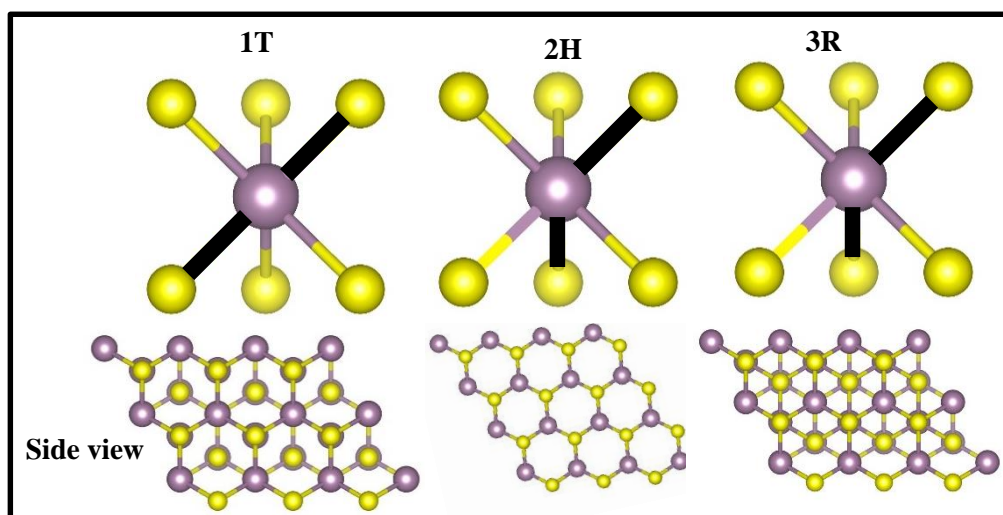


Figure 1.2 Schematic diagram of MoS₂ polytypes-1T, 2H, and 3R along with the side views.

Due to its abundances, large surface area, sheet-like structure, strong ionic conductivity, several valence states, unique electronic structure, and stable semiconducting properties, MoS₂ has received a lot of interest for testing its viability as an electrode material for energy applications. To date, different approaches have been introduced to prepare few-layered MoS₂ nanostructures using top-down and bottom-up techniques. The top-down approach uses exfoliation techniques as mechanical exfoliation, liquid-phase exfoliation, chemical intercalations, etc., while the CVD, PVD and hydrothermal synthesis processes are effective bottom-up methods for producing MoS₂ films or flakes. Thin flakes

of MoS₂ are produced from their parent bulk crystals via mechanical exfoliation. This method produces highly pure single-to few-layer flakes that can be used to create fundamental electronics. The difficulty to control the size and thickness as well as unsuitability of this method for large-scale applications are the main disadvantages. The bulk materials can be exfoliated utilizing number of mechanical processes such as sonication, shearing, stirring, grinding, and bubbling [48]. Liquid exfoliation is one of the common top-down approach, where to break down the cohesiveness between neighboring layers, the direct sonication process is used which depends on the solvent and/or surfactant. Therefore, the solvent must be selected so that its surface tension is close to the material's surface energy. The shape, size, and layering of the materials produced by this approach are random [48]. Mishra *et al.* synthesized few layer MoS₂ and WS₂ via sonication of their bulk powders in a soapy water as a solvent [49]. When compared to mechanical exfoliation, the yield of liquid exfoliation is significantly higher, however defective flakes are also found. The suitability of this method appears when large quantities of nanomaterials are required and defects do not significantly impair applications, such as in the production and storage of energy. This method offers a low-cost and straightforward technology for manufacturing 2D MoS₂ nanosheets on a large scale. Another significant and popular top-down strategy for the synthesis of few-layer nanostructures is the lithium intercalation method. Intercalation of ionic species is used in the liquid phase exfoliation method to exfoliate multilayer materials. This method is demonstrated by submerging a powder sample in a solution of n-butyl lithium to intercalate between the layers, followed by exposure to water. The water molecules react with lithium and produces H₂ gas, the evolved gas rapidly separates the layers of MoS₂ [50]. The material produced by this exfoliation technique differs structurally and electronically from its bulk equivalent.

Another, methods for synthesizing high-quality, large-area monolayers of 2D materials is the CVD method. Generally, it needs high-temperature heating and solid precursors. MoS₂ has been produced using CVD in a variety of ways, where different precursors undergo chemical reactions in the vapour state and the desired product is deposited as a solid-state thin film [17]. Sulfurizing a sputtered thin layer of Mo on wafer is another evaporation method used for synthesis of MoS₂ film [51]. The CVD methods has disadvantage such as high temperature, high vacuum, and certain substrates. The hydrothermal synthesis of MoS₂ has an advantage over other methods that it makes use of inexpensive precursors such as metal salts. A chemical reaction between the metal-salt precursors occurs during the procedure at a moderate temperature around 200 °C. Additionally, hydrothermal synthesis is a method that can be scaled up to produce MoS₂ nanosheets of excellent quality in the ideal size and thickness.

1.3.1 Properties and Applications of MoS₂ Nanostructures

Electrical Property

The indirect band gap of multilayer MoS₂ is known to be 1.2 eV, and it increases when the number of layers is reduced, reaching a direct band gap of 1.8 eV in single layer MoS₂. The mechanical strain affects the band gap of MoS₂ and changes it from direct to indirect band, which transforms the material from semiconducting to metallic. The atomic configuration and d orbital electron count of MoS₂ determine its electronic structure. So, MoS₂ characteristics are determined by the 4d and 3p orbitals in Mo and S, respectively [52]. Vikraman and the co-worker synthesized few-layer MoS₂ via chemical bath deposition and calculated a field-effect mobility value of $\sim 1.06 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [53]. Askari *et al.* synthesized n-type porous MoS₂ nanostructure using the hydrothermal reduction method and obtained carrier mobility $\sim 2.69 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [54].

Mechanical Property

A monolayer MoS₂ has high strength, flexibility and good elasticity with Young's modulus of 0.33 ± 0.07 TPa compared to its bulk structure with Young's modulus of 0.24 TPa [43]. The mechanical properties of common thermoplastic polymers (polyethylene, and polypropylene) can also be enhanced using few-layer MoS₂. Ge *et al.* synthesized free-standing film of MoS₂ incorporated with highly conductive poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate), which shows excellent fracture strength of 18.0 MPa and Young's modulus of 2.0 GPa [55].

Optical Property

The optical properties of MoS₂ depend upon the number of layers. The absorption coefficient and refractive index are the characteristics that indicate the optical response of a material. The MoS₂ has a higher light absorption coefficient (5 to 9% per layer) in the visible range compared to graphene (2.3 % per layer) [56]. Hashemi and the co-worker synthesized monolayer MoS₂ on inclined gold gratings and observed the maximum absorption up to 88% [57]. Nahid and co-workers synthesized MoS₂ nanosheets using the hydrothermal method and observed excellent photoresponsivity in the visible range with a maximum value of $\sim 23.8 \mu\text{A W}^{-1}$ using red laser [58].

1.4 Hydrogen Evolution Application

Although fossil fuels still dominate the world's energy landscape, sustainable energy technologies like wind and solar are becoming more and more appealing alternatives due to growing worries about the impact of anthropogenic carbon dioxide on the planet's climate. The deployment of these renewable energy sources has been hampered by the difficulties associated with energy storage and grid integration [59, 60]. In terms of clean energy carriers, hydrogen (H₂) is regarded as the best option because it has the high

gravimetric energy density $\sim 39 \text{ kWh kg}^{-1}$ of all chemical fuels and may greatly minimise carbon emissions. The molecular hydrogen is a vital chemical reagent needed for numerous industrial operations essential to maintaining human civilisation. The electrochemical water splitting is regarded as the most promising method for clean hydrogen production. Schematic of hydrogen evolution reaction **Figure 1.3**. This eco-friendly and efficient method has attracted tremendous attention as it produces no carbon dioxide and one of the promising strategies to achieve effective water splitting for hydrogen production is to develop earth-abundant electrocatalysts. The ideal catalyst for HER would have a Gibbs free energy near to zero indicating, hydrogen binding on the surface of catalyst should neither too weak nor too strong. Therefore, the future research of highly active electrocatalysts for HER will concentrate on developing materials that are affordable, highly active and earth-friendly [61–63].

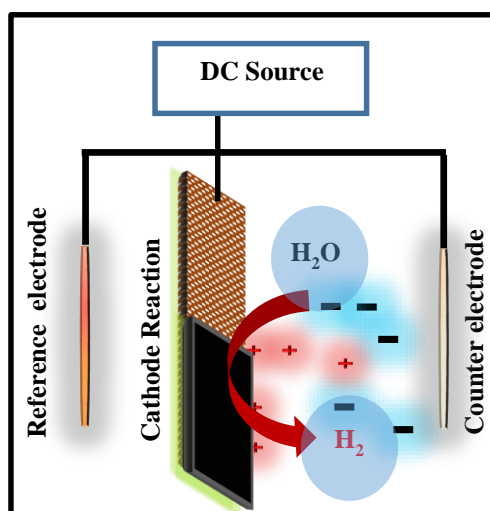


Figure 1.3 Schematic of hydrogen evolution reaction.

General Background

In water splitting process, oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) are typically the two half-reactions that make up the process, which can be described by following **equation 1.1-**



The electrolyte, cathode, and anode are the primary parts of an electrochemical water splitting cell. The OER takes place at anode, while HER occurs at cathode. An external voltage is applied across the electrodes to split water molecules into hydrogen and oxygen. The thermodynamic voltage of water splitting at 25 °C is 1.23 V regardless of the medium. To overcome the intrinsic activation barriers of electrodes and intrinsic resistances of the cell, it is necessary to apply voltages above the thermodynamic potential to perform electrochemical water splitting. This overpotential (η) is a result of increased resistance coming from the solution resistance and the contact electrode resistances. The following **equation 1.2** can be used to represent the real operational voltage (E_{op}) for water splitting.

$$E_{op} = \eta_a + \eta_c + \eta_{other} \quad (1.2)$$

The efficient water splitting requires reducing the total overpotential. First, improving the electrolytic cell design will contribute to lower the additional resistance η_{other} . Second, selecting an active catalyst for OER and HER, which will minimize the values of anode overpotential (η_a) and cathode overpotential (η_c). In the present work, we are focusing on active catalysts for HER process. It is critical to develop an active, acid stable, and earth-abundant electrocatalysts for HER. To analyse the efficiency for HER, three factors namely overpotential, current density at overpotential and Tafel slope of electrocatalyst are considered. The goal of electrocatalysis is to identify alternative, lower energy activation pathways that allow these electrochemical reactions to operate at a high current density and low overpotential. The reactions take place on the surfaces of catalysts, and adsorption/desorption occurs at the surface of electrocatalysts [64,65]. The overall electrode activity, the Tafel slope, stability, and faradic efficiency are some important metrics that used to explain the HER catalytic activity of specific catalyst material. The

general method for evaluating the activity of HER catalyst is observing the overpotential and Tafel's slope. To compare the overall electrode activity of various materials, two distinct potentials in the reaction are observed, the first one is the onset potential at which the current density is nonzero. The second one is the overpotential, usually the measured potential at which the current density is 10 mA cm^{-2} [66]. The value of these overpotentials can be evaluated using linear sweep voltammetry (LSV). The rate-determining step of the reaction is influenced by Tafel slope. The Tafel plot shows a nearly linear curve between logarithm of electrochemical current density (j) and applied potential. The high current density in Tafel plot denotes an easy electron transport at electrode/electrolyte interface with a low activation energy. Evidently, an active catalyst should display a low overpotential and a small Tafel slope [67,68]. The stability of catalyst represents a very significant complimentary aspect in the development of an industrially relevant catalyst. An estimation of whether the structural and catalytic properties of the electrode will remain stable for HER is given by the efficiency of a catalyst in the harsh electrolyte medium. The two types of stability studies are typically reported: (a) accelerated LSV test at high scan rates or (b) long term chronoamperometric tests [64,66].

Literature Review on Electrocatalysts for HER

Metals like Pt, Ru exhibit high activities towards HER in acidic electrolyte but are very expensive. Hence, much work has gone into finding alternatives that are cost-effective, earth-abundance and catalytic active. Different non-precious metal catalysts such as transition metal oxides, transition metal dichalcogenides, transition metal nitrides, transition metal phosphides etc. have been investigated as electrode material for HER. In order to obtain metal-free inexpensive HER catalyst, Li *et al.* utilized different functionalized carbon nanotubes such as EDA-MWCNTs and an ionic liquid AMMI-Br-functionalized MWCNTs and obtained a Tafel slope of 116 and 125 mV dec^{-1} , respectively, at a voltage

sweep rate of 2 mV s^{-1} [69, 70]. Mosconi and co-worker synthesized different Ni-doped MoS_2 nanostructures. They observed Tafel's slope of 64 mV dec^{-1} at a voltage sweep rate of 5 mV s^{-1} with 5% Ni doping in MoS_2 [71]. Sasidharan and co-worker synthesized Co_2P nanoparticles and investigated its electrochemical activity in acidic medium for HER [72]. Ren *et al.* have prepared porous tungsten nitride (WN) nanowires arrays by N_2 plasma treatment of WO [73]. As synthesized WN show enhanced HER electrocatalytic activity and stability in acidic medium. The fabrication of metal phosphides and nitrides suffer with tedious synthesis process along with lower yield of catalyst. Fan and co-worker showed Mo_2C on carbon cloth as active material for HER and obtained a Tafel slope of 124 mV dec^{-1} at a voltage sweep rate of 50 mV s^{-1} [74]. Liu *et al.* showed HER activity of NiCo_2S_4 nanowire on carbon cloth with Tafel slope of 141 mV dec^{-1} at a voltage sweep rate of 2 mV s^{-1} [75]. Zou and co-worker synthesized WSe_2 nanoflakes on carbon nanofiber and evaluated its catalytic activity. They obtained a Tafel slope of 98 mV dec^{-1} at a voltage sweep rate of 2 mV s^{-1} [76]. Wu *et al.* synthesized MoS_2 nanosheets using ball milling followed by thermal annealing process and showed Tafel slope of 68 mV dec^{-1} at voltage sweep rate of 2 mV s^{-1} [77]. Similarly, Wang *et al.* synthesized mechanically activated MoS_2 nanosheets using ball-milling method and obtained Tafel slope of 104 mV dec^{-1} at voltage sweep rate of 2 mV s^{-1} [78]. Voiry *et al.* synthesized 2H- MoS_2 nanosheets using chemical exfoliation and synthesized nanosheets show the Tafel slope of 75 mV dec^{-1} [79]. Kong *et al.* synthesised vertical MoS_2 nanostructure and tested its electrochemical activity towards HER and obtained Tafel slope of 75 mV dec^{-1} at current density of 2 mV s^{-1} [80]. In this thesis work, we have demonstrated the high electrocatalytic performance of different MoS_2 nanostructures (nanocluster, nanosheets and nanoflowers) based electrodes for HER in acidic media.

1.5 Supercapacitor Applications

Energy storage technologies like supercapacitors has drawn more interest due to their fast charging-discharging capability, easy operation and long cycle life [81]. It appears to be one of the main contenders to satisfy the growing demands of energy storage systems in consumer electronics, industrial power, public transport, and military equipment. Supercapacitors have recently been used in emergency doors on Airbus A 380 aircraft, demonstrating their safe and dependable performance. The energy density of a commercial supercapacitor is between 5 and 10 Wh kg⁻¹, which is much higher than that of normal dielectric capacitors (~ 0.2 Wh kg⁻¹) but much lower than that of conventional batteries (~250 Wh kg⁻¹) [82,83]. Thus, there is still a long way to go to increase the energy density of supercapacitors to match the batteries. A comparison of key properties of SCs with conventional capacitors and batteries are outlined in **Table 1.1** [84–86].

Table 1.1 Comparison of Key Properties of Capacitor, Supercapacitor, and Battery.

Functions	Capacitor	Supercapacitor	Battery
Time of charging	10 ⁻⁶ to 10 ⁻³ s	0.3 to 30 s	1 to 5 h
Number of cycles	Almost infinite	1 million	500-1000
Energy density (Wh kg ⁻¹)	<0.1	1-10	10-100
Power density (W kg ⁻¹)	>100,000	10,000	<1000
Coulombic efficiency (%)	Almost 100	>100	70-80
Charge storage determinants	Electrode area and dielectric	Microstructure of electrode & electrolyte	Thermodynamics and active mass
Operating temperature (°C)	-20 to 100	-40 to 85	-20 to 65

Fundamentals and Charge Storage Mechanism of Supercapacitors

Supercapacitors are mainly classified into two categories, according to their charge-storage mechanism: electrochemical double-layer capacitors (EDLCs) and pseudocapacitors [87–89]. The working principle of EDLCs is like conventional capacitors, where the energy is stored via physical adsorption of electrolyte ions at the surface of a porous electrodes during charging of the device. Owing to their high surface area and very short charge separation distances, EDLCs possess higher energy density than the conventional dielectric capacitors. As shown in **Figure 1.4 (a)**, EDLCs consists of two carbon electrodes dipped in a suitable electrolyte (KOH, H₂SO₄, Na₂SO₄, etc.) and an ion-exchange membrane situated between the electrode [90]. The capacitance of an EDLC electrode can be predicted according to following **equation 1.3** [91]-

$$C = \frac{\epsilon_r \epsilon_0}{d} A \quad (1.3)$$

where ϵ_r is the dielectric constant of the electrolyte, ϵ_0 is the permittivity of free space, d is the effective charge separation layer from electrodes (few to several Å) and A is the accessible surface area of the electrode materials. The EDLCs may store significantly more electric energy than typical dielectric capacitors due to their larger effective surface area (A) and nanoscale charge separation distance (d).

The concept of first EDLCs model was described by Hermann von Helmholtz in 1853. According to this model, when an electrical conductor is immersed in an electrolyte, the opposite charges are accumulated at the interface of the electrode/electrolyte and form the double layer separated by an atomic gap. This layer is known as compact or Helmholtz layer, as shown in **Figure 1.4 (b)** [92]. Further, the Gouy-Chapman modified the over simplified model of rigid charged surface and contemplated the diffuse layer which arises due to the thermal motion of electrolyte ions. However, the model fails to explain the

formation of highly charged double layers at the electrode/electrolyte interface. The Otto Stern later integrates the essentials of both Helmholtz-Perrin and Guoy-Chapmann electrical double layer theories. According to this theory, the double layer has two distinct ion distribution regions. The first region is approximately single ion thick, and these ions are firmly adsorbed to the solid surface and form the inner Helmholtz plane (Helmholtz view) [93,94]. The remaining charges are distributed through the electrolyte next to the compact layer as a diffuse layer (Guoy's view) and called outer Helmholtz plane (OHP). So, the Stern model suggest that because of thermal agitation, a part of ions in solution are fixed to the electrode and the rest are scattered in cloud like pattern, as shown in **Figure 1.4 (b)**. In the case of SCs, the charge accumulation mechanism is based on the surfaces rather than the bulk volume. At the time of charging, anions of electrolyte (A^-) travel towards positive electrode (E_1) and the electrochemical charging process can be expressed as- $E_1 + A^- = E_1^+ // A^- + e^-$, where // represents the electrode-electrolyte interface. During discharging, cations (C^+) of electrolyte moves towards negative electrode (E_2) and the electrochemical discharging process can be expressed as- $E_2 + C^+ + e^- = E_2^- // C$.

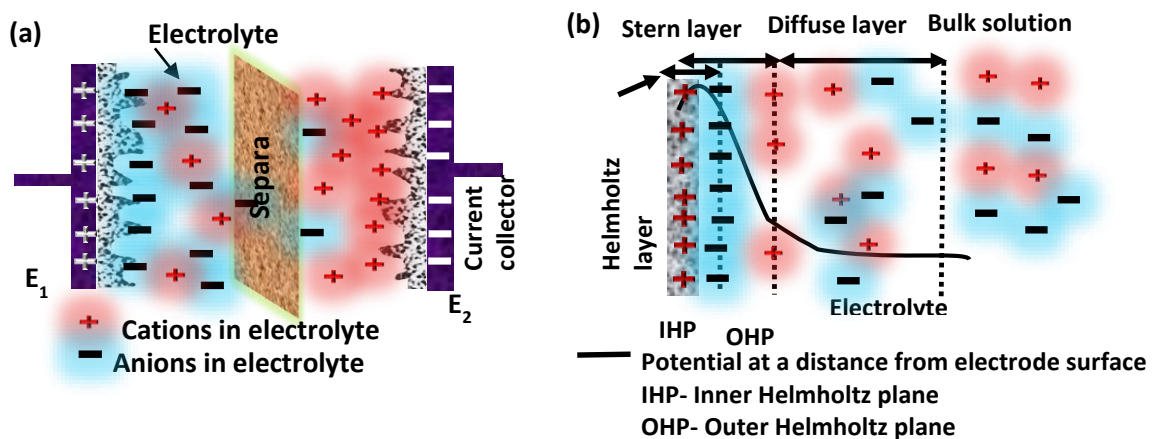


Figure 1.4 (a) Schematic illustration of electrochemical double layer capacitor, (b) The Charge storage mechanism of the electrochemical double-layer capacitor.

The word pseudocapacitance was coined by Conway to identify those materials that display electrochemical signatures (CV and CD) which are close to those of typical EDLC

[95]. Unlike EDLCs, pseudocapacitors involve a different charge storing mechanism. Pseudocapacitors store electric energy through reversible redox reactions, which occur at the electrode/electrolyte interface involving the passage of charges between electrode and electrolyte [96]. The electrochemical charging process is expressed as- $E_1 + A^- = E_1^{\delta+} // A^- + \delta e^-$, while the discharging process is expressed as- $E_2 + C^+ + \delta e^- = E_2^{\delta-} // C^+$, where E_1 and E_2 are positive and negative electrodes and the parameter δe^- represents electrosorption valence, related to oxidation-reduction reactions. The metal oxides, such as RuO_2 , NiO and MnO_2 , as well as conducting polymers (poly-pyrrole and polyaniline) are classic examples of redox pseudocapacitive materials [97]. In such redox pseudocapacitor devices, the capacitance is determined by the reactant ions and active site density and the maximum achievable capacitance value is around 5000 F cm^{-3} [98]. The EDLCs have advantage of good cyclic stability and high-power density, while pseudocapacitors offer high-energy density. The operating temperature of a device is a crucial factor the thermal stability of SCs can be improved by selecting appropriate electrode and electrolyte materials.

Literature Review on Electrode Materials for Supercapacitors

The potential benefits of supercapacitors include greater power densities, faster charge-discharge rates, cyclic stability, and risk-free operation. However, the main challenge with supercapacitors technology is how to boost energy density without sacrificing power density and security. This inspires the researcher toward designing and preparing many novel electrode materials with various structures. The carbon and TMDCs nanomaterials stand out as electrode materials due to their physicochemical stability, unique pore structure, facile large-scale synthesis, along with the presence of accessible electrocatalytic active sites [97], [99–103]. The high specific surface area ($1000\text{-}3000 \text{ m}^2 \text{ g}^{-1}$) of carbon nanomaterials can theoretically rise to double-layer capacitances of $300\text{-}550 \text{ F g}^{-1}$ [90,91]. The carbon nanostructures like activated carbon, carbon aerogel, CNT,

graphene etc. with high specific surface area, meso-porosity and good electrical conductivity show good EDLC behaviour, but experimentally achieved specific capacitance of these materials are low due to limited accessibility of surface sites. Xie *et al.* synthesized hierarchical porous carbon microtubes via carbonization and consecutive KOH activation process and as synthesized material showed capacitance of 292 F g^{-1} at a current density of 1 A g^{-1} in 6 M KOH aqueous solution [104]. Kim and coworkers demonstrated considerable electrochemical performance of 108 F g^{-1} at slow scan rate of 1 mVs^{-1} for nitrogen-enriched ordered mesoporous carbon nanopipes in $1 \text{ M H}_2\text{SO}_4$ electrolyte [105]. Chen *et al.* investigated nitrogen-doped carbon nanofibers (CNFs) coated with polypyrrole (CNFs@polypyrrole) for supercapacitor application. They reported high specific capacitance of 202 F g^{-1} at discharge current density of 1 A g^{-1} in 6 M aqueous KOH electrolyte [106]. Stoller *et al.* synthesized rGO nanostructure and utilized it for supercapacitor application. They demonstrated specific capacitance of 135 F g^{-1} with 5.5 M KOH electrolyte at current density around 1 A g^{-1} [107]. Rajagopalan *et al.* demonstrated specific capacitance of KOH treated rGO in acidic medium ($2 \text{ M H}_2\text{SO}_4$) and showed the capacitance value of 253 F g^{-1} at current density of 0.2 A g^{-1} [108]. Apart from pristine carbon nanostructures, metal oxides, conducting polymers and their nanocomposites with carbon nanostructures have been explored as pseudocapacitive electrode materials [97], [109–111]. These materials can provide multiple oxidation states for efficient redox reaction at the electrode surface, and this may allow pseudocapacitor to achieve high energy density and capacitance. Gujar and co-worker synthesized crystalline RuO_2 structure via electrochemical deposition method and showed specific capacitance of 498 F g^{-1} at a scan rate of 5 A g^{-1} [112]. Mishra *et al.* synthesized $\text{RuO}_2/\text{graphene}$ nanocomposite and showed specific capacitance $\sim 265 \text{ F g}^{-1}$ at 10 mV s^{-1} [97]. Apart from these materials, recently TMDCs nanostructures have also been explored as electrode materials for supercapacitors.

Li *et al.* synthesized hollow MoS₂ nanospheres and showed a specific capacitance of 142 F g⁻¹ at a current density of 1 A g⁻¹ with 1M Na₂SO₄ electrolyte [113]. Zhou *et al.* showed specific capacitance of 122 F g⁻¹ at 1 A g⁻¹ for MoS₂ nanoflowers in 1M KCl as electrolyte [114]. Soon *et al.* showed CVD grown edge oriented MoS₂ film with specific capacitance up to 100 F g⁻¹ at slow sweep rate of 1 mV s⁻¹ in acidic electrolyte (0.5 M H₂SO₄) [115].

1.6 Scope and Objective of the Present Work

In view of recent ecological issues, scientific community is tremendously encouraged to develop sustainable and renewable energy devices to meet the growing demand for energy supplies. The hydrogen generation and supercapacitors can provide the solutions for energy generation and storage for meeting global energy demand. The rGO and MoS₂ possess some attractive properties such as, layered structure, high conductivity, high-surface area, flexibility, and good stability in acidic/basic medium. These characteristics allow rGO and MoS₂ nanostructures to be used for energy generation and storage. The MoS₂ is a potential catalyst for HER due to its highly active edge site, tuneable morphology, abundance, and low cost. Hence, understanding of electrocatalytic behaviour of MoS₂ is important for its application in energy generation application. The unique physical and chemical properties, sheet like morphology of rGO and MoS₂ nanostructures facilitate the double-layer charge storage while defects and oxygen-functionality facilitate charge transfer at electrode/electrolyte interface. Although, there have been few studies on rGO and MoS₂ for supercapacitor applications, the comparative study of these materials in acidic and basic electrolyte is still lacking. Here, we examine their suitability with aqueous and solid (acidic and neutral as well) electrolytes for supercapacitor applications. The main objectives of the present work are as follows-

- ❖ Successful synthesis of rGO and different morphologies for 2H MoS₂ nanostructures via hydrothermal technique and their characterization.
- ❖ Investigation of electrocatalytic behaviour of prepared rGO, MoS₂ nanostructure and MoS₂-rGO heterostructure for HER.
- ❖ Investigation of capacitive behaviour of rGO, MoS₂ nanostructure and MoS₂-rGO heterostructure electrodes in neutral (1M Na₂SO₄) and acidic (1M H₂SO₄) electrolytes.
- ❖ Performance study of rGO, MoS₂ nanostructure and MoS₂-rGO heterostructure based solid-state supercapacitor device with neutral (PVA-Na₂SO₄) and acidic (PVA-H₂SO₄) solid electrolytes.