Advanced Transition Metal Dichalcogenides Catalysts for Energy Conversion and Storage systems

BY

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THESIS

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The results and discussions in this thesis are copied from my published or under review papers with written permission from the journals only for published papers (see appendix). Below, the contributions of all the co-authors are listed:

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LIST OF ABBREVIATIONS AND NOMENCLATURE

2D	two-dimensional
3D	three dimensional
ABF	annular bright field
AFM	atomic force microscopy
AM	air mass
AN	accepter number
AP-CVD	ambient-pressure chemical vapour deposition
CA	chrono-Amperometry
C _{dl}	double layer capacitor
CE	counter electrode
CNT	carbon nano tubes
Co-OEC	cobalt-oxygen evolution catalyst
CV	Cyclic voltammetry
CVD	chemical vapor deposition
CVT	Chemical vapor transport
DEMS	differential electrochemical mass spectroscopy
DLS	dynamic light scattering
DME	Dimethoxyethane
DMSO	dimethyl sulphoxide
DOS	density of states
EBL	electron beam lithography
EDX	energy dispersive X-ray spectroscopy
EELS	electron energy loss spectra
Ef	fermi energy level
EIS	electrochemical impedance spectroscopy
EMIM-BF ₄	1-ethyl-3-methylimidazolium tetrafluoroborate
F.E	Faradaic efficiency
FFTs	fast Fourier transforms
GC	glassy carbon
GDL	gas diffusion layer
HAADF	high-angle annular dark-field
HER	hydrogen evolution reaction
HRTEM	high resolution transmission electron microscopy
IL	ionic liquid
IPA	isopropyl alcohol
ITO	indium titanium oxide
KO	potassium hydroxide

	low angle annular dark field
	local density of states
	Li O lithium penevide
	Li ₂ O ₂ lithium peroxide
	LiO ₂ lumum superoxide
LIIFSI	bis(1filluoromethanesullonyi) imide
MeOH	methanol
NFS	nanoflakes
NIR	near infra-red
NPs	nano particles
OER	oxygen evolution reaction
ORR	oxygen reduction reaction
PDOS	projected density of states
PEO	poly(ethylene oxide)
PFK	perflourokerosene
ppb	parts per billion
ppm	parts per million
PV	photovoltaic
QM/MM	quantum molecular dynamics
R _{ct}	charge transfer resistance
RDE	rotating disk electrode
RDS	rate determining step
RE	reference electrode
RF	roughness factor
rGO	reduced graphene oxide
RHE	reversible hydrogen electrode
SAED	selected area electron diffraction
sccm	standard cubic centimeter
SEAD	selected area electron diffraction
SEM	secondary electron multiplier
SEM	scanning electron microscopy
SFE	solar to fuel
STEM	scanning transmission electron microscopy
SWCNT	single-walled carbon nanotube
TCD	termal Conductivity Detector
TEGDME	tetraethyleneglycol dimethylether
TEM	transmission electron microscopy
TMD	transition metal dichalcogenides
TMDC	transition metal dichalcogenide
TOF	turnover frequency
UHP	ultra-high purity
~	mon panty

UHV	ultra-high vacuum
UPS	ultraviolet photoelectron spectroscopy
VA	vertically aligned
V _{oc}	open circuit voltage
WE	working electrode

SUMMARY

Energy conversion and storage systems could provide a viable route to store energy in the form of the chemical bond. In general, energy can be stored or converted into chemical bonds through electrochemical and photo-electrochemical processes such as Li-oxygen (Li-O₂) batteries, fuel cells, hydrogen (H₂) generation, carbon dioxide (CO₂) reduction reactions and utilized as an energy source in the form of electricity or fuel. However, these systems have advanced far more slowly over the last two decades due to the lack of a suitable catalyst. Fundamentally, the electronic structures of the existing catalysts are not well suited for electrochemical reactions mainly due to their high work function and low density of d-orbital electrons near the fermi level of energy.

Here for the first time we report that the inexpensive non-noble-metal transition metal dichalcogenide (TMDCs) family of catalysts performed remarkably well for any electro and photo chemical reactions owing to their advantageous electronic structure. The performance of these materials was also promoted by using an appropriate electrolyte, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄), as a reaction medium. In particular, the synergetic effect between the ionic liquid (IL) and the catalyst enhances the electrochemical reaction at the TMDC edge atoms where the IL plays multiple roles to facilitate the reaction pathway. We studied the performance of TMDC family for H₂ generation, CO₂ reduction reactions for energy storage systems. Moreover, we introduce a

new generation of energy storage systems, a lithium oxygen (Li-O₂) battery with five-fold higher energy density using a molybdenum disulfide/EMIM-BF₄ co-catalyst system.

Details are discussed into three separate chapters entitled "Hydrogen evolution reactions (HER)", "CO₂ reduction reactions" and "Li-O₂ battery" due to different technical characteristics of each system.

In brief, the state-of-the-art of systems for H₂ generation, CO₂ reduction and Li-O₂ battery were discussed in the first chapter. In the second chapter, the chemical vapor deposition (CVD) method has been employed to synthesize crystalline 3D structured molybdenum disulfide (MoS₂) with bare Mo edge atoms on graphene film, and demonstrated its outstanding activity and stability for the hydrogen evolution reaction (HER). In the third chapter, a novel 2D form of transition metal dichalcogenide (TMDC) has been used for catalyzing CO₂ reduction in the ionic liquid 1-ethyl-3methylimidazolium tetrafluoroborate (EMIM-BF₄) environment. Finally, in chapter 4, the concept of co-catalyst system is introduced in the Li-O2 batteries for the first time. In more details, it has been shown that MoS_2 nanoflakes (NFs) in the ionic liquid (IL) 1-ethyl-3methylimidazolium tetrafluoroborate (EMIM-BF₄) exhibits unique bi-functional catalytic activity for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). This MoS₂/IL system is also found to perform remarkably well in a Li-O₂ battery system with a high round trip efficiency, small discharge/charge polarization gap and good reversibility.

1. CHAPTER 1: Introduction

The global energy demand has been predicted to increase by one-third during next few decades. This demand largely relies on the fossil fuels (e.g., gasoline) that are limited in nature and cause severe environmental issue[1], [2]. Therefore there is an urgent call to develop advanced environmentally friendly and inexpensive energy conversion and storage systems to overcome this energy demand.

In general, the energy can be stored or converted into the chemical bonds through the electrochemical and photo-electrochemical process i.e., batteries (Li-oxygen), fuel cells, hydrogen (H₂) generation, carbon dioxide (CO₂) reduction reactions and utilized as an energy source in the form of electricity or fuel[2]–[4]. In the next section, we review the recent literature on hydrogen evolution reaction (HER) and CO₂ reduction reaction as energy conversion systems. We will also review lithium-oxygen (Li-O₂) battery system which is known as the most efficient energy storage system.

1.1. Literature review of HER systems

Hydrogen evolution reaction (HER) are promising in the field of energy conversion systems that produce hydrogen as a green fuel. To date, several synthetic structures, such as MoS₂ nanoparticles on Au (111)[5], vertically aligned MoS₂ nanoflakes[6], ordered double-gyroid MoS₂ bi-continuous networks[7], defect-rich MoS₂ nanosheets[8], and chemically synthesized thiomolybdate [Mo₃S₁₃]²⁻ clusters[9] have been developed and tested for HER. However their performance is still far from platinum which is known as

the best catalyst for HER. The main drawback of these systems is that of high overpotential (110-180 mV vs RHE)[9] and low turnover frequency (TOF< 3.5)[9], [10]. This is mainly attributed to the low number of active edge sites and high charge transfer resistance toward the catalyst edge site. Ultra-high vacuum (UHV) deposited MoS₂ nanoparticles on Au (111) is an exception[5]. However its synthesis route is not scalable due to technical limitations associated with UHV growth. The stability of the catalysts is another challenge of the existing HER catalysts. Therefore, finding an advanced catalyst with low charge transfer resistance and high number of active edge sites that remains stable during the long term HER is essential to make this process energy and cost efficient.

1.2. Literature review of CO₂ reduction systems

Carbon dioxide (CO₂) is known as the most abundant waste gas and also very stable molecule on earth [11], [12]. The conversion of CO₂ into energy rich products such as syngas (a mixture of CO and H₂), ethylene, methanol, or formic acid is desired using renewable sources of energy (i.e. solar, geothermal, wind, etc.)[13], [14]. Energy-rich chemical fuels can be burned anytime anywhere. Among various techniques, electro and photo electrochemical CO₂ reduction are a viable route to convert CO₂ into useful fuels (e.g., syngas, methane and ethylene) but thus far the results have been hindered because of the lack of a suitable and affordable catalyst that can selectively reduce CO₂ at low enough over-potentials.

The products of CO₂ reduction are mainly dependent on the metal catalysts[15]–[19], the electrolyte[15]–[18], [20]–[22] and cathode polarization used in the process. According to Hori's reports[15]–[18], [20]–[22], in aqueous solution, metallic In, Sn, Hg and Pb are selective for formation of formic acid, metallic Zn, Au and Ag produce carbon monoxide, and metallic Cu produces hydrocarbon, aldehydes and alcohols. In non-aqueous solutions[15]–[18], [20]–[22], Pb, Ti and Hg produce oxalic acid, Cu, Ag, Au, Sn, In, Zn can form carbon monoxide and carbonate ions, Ni, Pd, and Pt are selective for carbon monoxide formation, and Al, Ga, and group III (except Ni, Pd and Pt) can produce carbon monoxide and oxalic acid. Despite the high catalytic efficiency of most of these metals to produce useful products, previous studies have shown that the reduction of CO_2 must take place at large over-potentials mainly due to high activation energy of $(CO_2)^{-1}$ intermediate formation [23]-[26]. This occurs since the first step in CO₂ reduction is the single electron reduction that requires a large reorganizational energy between the linear molecule and the bent radical anion. This step has always required applying large electrical voltages to CO_2 to make the change. That excess voltage is an energy loss, meaning that the conversion process requires far more energy to create a useful product than what can be stored in its chemical bonds. This step is also a rate-determining step for CO_2 reduction. Add to this, in aqueous electrolytes, CO₂ reduction competes with the hydrogen evolution reaction (HER) in which both of them consume protons to form final product[23]–[28].

1.3. literature review of Li-O₂ battery

In a quest to find an efficient electrical energy storage systems, metal-oxygen batteries (e.g., lithium, sodium etc.) are considered as a feasible approach due to their high specific energy[29]–[31]. The theoretical specific energy of lithium oxygen (Li-O₂) batteries is one order of magnitude higher than that of commonly used Li-ion batteries[29]–[31].

Fundamentally, the specific energy and rechargeability of Li-O₂ batteries are governed by the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) rates at the cathode and their corresponding overpotentials[3], [29]–[31]. Recent efforts in the field of Li-air battery have shown the promising potential of this technology in the area of energy storage systems[3], [30]–[33]. However, Li-air battery development is still in its early stage and faces many challenges including the low energy deficiency (large potential gap between charging and discharging), lack of stability, poor capacity and inadequate rechargeability etc[33]–[35]. To overcome these challenges, effective catalyst combined with an electrolyte that can effectively work together for both ORR and OER is essential.

In search of an appropriate electrolyte, various non-aqueous electrolytes (organic carbonates, polymers, glymes and ILs) have so far been tested in Li-air battery. It was noticed that organic carbonates can be decomposed above the required potential for charging. Additionally, the intermediate oxygen radical anion O_2^{-} formed during ORR process[14], [36], [37] can also decompose the organic carbonate solutions.

Dimethoxyethane (DME) is also oxidatively unstable during the charging-discharging cycle[38]. Polymer electrolytes e.g., poly(ethylene oxide) (PEO) with a lithium salt exhibit acceptable stability but they also have weak ionic conductivity resulting in poor performance of Li-air battery[39]. However, ILs, dimethyl sulphoxide (DMSO) and glymes are found to be significantly stable electrolytes due to the absence of less stable carboxyl groups[40]–[43].

To reach the theoretical charge density limit, enormous efforts have been further attempted towards the finding of highly active catalysts as a cathode. In this respect, carbon materials have been widely studied in different forms including carbon black, carbon nanofibers, nitrogen doped carbon and graphene[44]–[47]. It has been argued that the catalytic activity of carbon electrode is mainly governed by the density of the defects, surface area, pore size and volume etc[44], [47]. For instance, hierarchically porous graphene has shown relatively high discharge capacity (15000 mAh/g_{carbon}) mainly due to their high porousity[44].

In general, non-functionalized carbon based materials do not exhibit strong catalytic properties for ORR/OER. Thus hybrid catalysts were studied by depositing catalytically active materials (e.g., Pd, RuO₂, Co₃O₄, α -MnO₂ etc.,) on the carbon electrodes[48]–[52]. Such structure e.g., RuO₂/CNTs has shown significantly enhancement (up to 73%) in the electrical efficiency. It has been claimed that RuO₂ nanoparticles contribute to the formation of poorly crystalline lithium peroxide (Li₂O₂) during ORR which can be

efficiently decomposed at low potential upon OER[51]. Similarly, RuO₂/graphene also exhibits significant performance at 3.7 V (average charge potential) with high specific capacity of 5000 mA h g⁻¹. [53] Instead of RuO₂, Co₃O₄ nanocrystals were directly grown on nitrogen doped reduced graphene oxide (N-rGO) and their performance was tested for ORR and OER. This hybrid catalyst showed substantial ORR catalytic activity similar to Pt but ~ 40 times higher OER activity compared to the Pt catalyst. It has been argued that the unusual catalytic activity of hybrid catalyst originated from the synergetic chemical coupling effects between Co₃O₄ and graphene[54] but their ORR and OER mechanisms remain unclear. In another report, α -MnO₂/rGO hybrid catalysts evidenced higher specific capacity (~11000 mAh.g⁻¹) and lower discharging and charging voltage gap (~1.1V)[52]. It was shown that not only the type of the catalyst but also crystal structure of the catalyst plays important role in improving the battery performance. As an example, α - and β -MnO₂ nanowires - differed in surface area by less than a factor of two - yet the former shows one order of magnitude higher discharge capacity [55]. The hollandite type crystal structure of a-MnO₂ consists of 2×2 tunnels formed by edge- and corner-sharing MnO₆ octahedra allows to accommodate both Li^+ and O_2^- within the tunnels which is not possible in the other MnO_x materials.

To decrease the charging-recharging potential gap, bi-functional hybrid catalysts were made of two different elements- one for ORR and another for OER. For example, tetragonal CoMn₂O₄ spinel nanoparticles were directly grown on the surface of graphene sheets. It was noticed that intrinsic catalytic activity of Co and Mn for the OER and ORR can reduce the charging-discharging potential gap to ~0.3 V[56]. Pt-Au nanoparticles as bi-functional catalyst also significantly reduce the voltage gap between the ORR and OER to less than 0.8 V[57]. During ORR, the discharge voltage was comparable to that of Pt/C, but the charge voltages was 3.4 to 3.8 VLi, slightly lower than obtained for Au catalyst. In another effort, α -MnO₂ was combined with Pd and the energy efficiency was significantly improved from 60 to 89%[58]. Effect of the catalyst size has also been studied and it has been elucidated that the discharge–recharge voltage gap of nano TiN was approximately 390 mV smaller than that of micro-TiN at 50 mAh/g[59].

Recently, attention has turned to carbon free catalysts since carbon materials can be decomposed during oxidation of Li_2O_2 resulting in severe polarization, capacity fading on cycling and early cell death. In this respect, different carbon free cathodes e.g., nanoporous gold[34], titanium carbide (TiC)[60] were also examined. Nano-porous gold catalyst based Li-air battery exhibits excellent performance and retained approximately 95% capacity even after 100 cycles but the capacity was relatively modest (~300 mAhg⁻¹). Comparatively a four times lighter titanium carbide (TiC) has also shown superior stability (98% capacity retention after 100 cycle) but low capacity and high charging- discharging potential gap are major issues to be overcome[60].

1.4. Research objective

The review of the existing systems for energy conversion and storage systems specially H₂ generation, CO₂ conversion and Li-air battery demonentsrate that many physical and

chemical approaches have been employed to enhance the catalytic performance of these systems. However, advancements have been slowled over the last two decades, mainly due to lack of suitable and affordable catalysts.

In the quest for a cost effective and efficient catalyst for these systems, we recently identified a new class of catalysts that perform remarkably well in any electro and photo electrochemical reactions. We discovered that the inexpensive transition metal dichalcogenide (TMDCs) family of catalysts performed well for hydrogen generation, CO₂ reduction reaction and Li-air battery systems with low over-potential and extremely high reduction reaction rate. The electronic property of these materials is also tuned using the appropriate electrolyte i.e., 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) for CO₂ reduction reaction and Li-O₂ battery system. In particular, in more complex reaction systems (e.g., CO₂ reduction reaction and Li-O₂ battery) the synergetic effect between the ionic liquid (IL) and the catalyst enhances the electrochemical reaction at the TMDC catalyst edge sites where the IL plays multiple roles in facilitating the reaction pathway. The details are further discussed in three separate chapters entitled "Hydrogen evolution reactions", "CO₂ reduction reactions" and "Li-air battery" due to different technical features of each system.

2. CHAPTER 2: Hydrogen evolution reactions

2.1. Introduction

Molybdenum disulfides (MoS₂) has been widely used in a broad range of applications from electronics[61], [62] and optoelectronics[63], [64] to energy conversion[7], [10] and storage systems.[65] Although enormous attention has been dedicated to produce atomically thin two dimensional (2D) MoS₂ films,[66]–[71] layered three dimensional (3D) structures of MoS₂ with a high density of active edge atoms for electrochemical applications have not yet been explored.

To date, several synthetic structures, such as MoS_2 nanoparticles on Au (111),[5] vertically aligned MoS_2 nanoflakes,[6] ordered double-gyroid MoS_2 bi-continuous networks,[7] defect-rich MoS_2 nanosheets,[8] and chemically synthesized thiomolybdate $[Mo_3S_{13}]^{2-}$ clusters[9] with sulfided Mo edge atoms have been developed and tested for HER. In this report, we employed the chemical vapor deposition (CVD) method to synthesize crystalline 3D structured MoS_2 with bare Mo edge atoms on graphene film, and demonstrated its outstanding activity and stability for HER. In particular, the electrochemical impedance spectroscopy (EIS) experiments and density functional theory (DFT) calculations reveal that Mo edge terminated MoS_2 and graphene show strong synergy for HER resulting in significant enhancement in the electron transfer to the reactants and desorption of intermediates from catalyst surface.

2.2. Material synthesis and characterization

The 3D structure of MoS₂ was synthesized through a dual precursor CVD method with two separated zones to precisely control the temperature profile of the growth process. Seven milligrams of MoO₃ powder was uniformly dispersed inside of the crucible to produce a uniform concentration of MoO₃ vapor all over the target substrate. The upsidedown target substrate also mounted on top of the MoO₃ crucible. A sufficient amount of sulfur (S) precursor (one gram) is also located in the upstream of the flow to guarantee complete sulfurization. Independent two-stage temperature profiles (Figure 1) were applied to each zones to synchronize the evaporation time of the S and MoO₃ powders to avoid the formation of intermediate structures. More details of CVD synthesis process is discussed in the section 2.2.1.

2.2.1. Details of Material Synthesis

Two alumina crucibles, one containing 7 milligrams of MoO₃ powder (Sigma-Aldrich, 99.98%) and the other containing 1 gram of sulfur powder (Sigma-Aldrich, 99.98%) are used as precursors for MoS₂ growth. The sulfur crucible is placed in the upstream of the furnace where the maximum temperature reaches 300°C, while the MoO₃ crucible is located in the center of the tube with a maximum temperature of 850°C. The target substrates are loaded upside down on top of the MoO₃ crucible. Prior to running the temperature profile, the chamber is first evacuated down to 1 mtorr and then purged by argon flow to reach the atmospheric pressure. During the growth process in atmospheric

pressure, 200 standard cubic centimeter (sccm) of argon flows in the chamber. The sulfur evaporation rate is sharply increased from 100°C to 300°C with rate of 10 °C/min as soon as the temperature of the central zone reaches 720°C. Afterwards, the central temperature is ramped up to 850°C and is kept constant for 15 minutes. Finally, the furnace is cooled down to the room temperature by natural air convection. During the cool down process, the sulfur evaporation continued for about 10 minutes after the MoO₃ evaporation had stopped.



Figure 1. Temperature profile for MoO₃ and sulfur zone

2.2.2. Details of Material Characterization

Figure 2a shows the low magnification scanning electron microscopy (SEM) image of the 3D MoS₂ structures. The atomic structure of the 3D MoS₂ and its edge structure are also shown in Figure 2b using scanning transmission electron microscopy (STEM). A multi-layered stacking of MoS₂ nanosheets shown in Figure 2b with Mo terminated edges along the (100) and (010) crystallographic planes is similar to the previously reported edge

terminations in mechanically exfoliated MoS₂.[2] The corresponding fast Fourier transforms (FFTs) taken from multi-layers area (inset of Figure 2b) shows sharp hexagonal benzene-like patterns indicative of highly crystalline 3D structures with epitaxial stacking of the MoS₂ layers. X-ray photoelectron spectroscopy (XPS) results (Figure 2c) show standard Mo $3d_{5/2}$ (~229.0 eV) and S $2p_{3/2}$ (~162 eV) peaks consistent with the presence of Mo^{IV} and the S²⁻ present in MoS₂ structures. The XPS spectrum without any peaks at ~236 (a characteristic for Mo^{VI}) illustrates absence of molybdenum oxides.[72]In addition, Figure 2d demonstrates Raman point spectra obtained from the 3D MoS₂ structure up to 800 cm⁻¹. Results indicate that MoS₂ characteristic peaks associated with E_{2g} and A_{1g} vibrational modes for 3D structured MoS₂[73] without any other peaks up to 800 cm⁻¹



Figure 2. (a) Low magnification SEM image from 3D structured MoS_2 (scale bar is 15 μ m). (b) Atomic-resolution ADF STEM image, showing the layered structure of the 3D crystals (scale bar is 3 nm). The inset shows the fast Fourier transform (FFT) obtained from the multilayer region in which the unique hexagonal pattern of MoS_2 crystal implies the epitaxial stacking of the layers. (c) XPS spectra of the 3D MoS_2 structure showing sulfur peak (Mo peak is shown in the inset). (d) Raman Point spectra obtained from a 3D structured MoS_2 .

Energy dispersive X-ray spectroscopy (EDX) results (Figure 3) obtained from the 3D

structures reveals an approximate composition of 32% Mo and 68% S, which is consistent

with the stoichiometric ratio of MoS₂. [75]



Figure 3: Representative EDX spectrum of MoS_2 flakes. Inset: atomic percentage of the molybdenum and sulfur which is extracted from deconvolution of the molybdenum and sulfur EDX peak.

In order to visualize the layered construction of the CVD grown 3D MoS₂, we quenched the CVD chamber by force cooling to rapidly reduce the temperature and terminate the growth of the top layers. High magnification SEM images of the resulting structure (Figure 4) not only show the layered construction of the 3D grains, but also reveal an epitaxial conformance between the layers, as evidenced by the parallel edges in the stacked layers. This is consistent with the FFT patterns of the atomic resolution images obtained from STEM.



Figure 4: SEM image of the 3D structured MoS2 from a rapid cooling experiment (scale bar is $0.5 \ \mu m$).

To gain insight into the growth mechanism of the 3D MoS₂, we deliberately placed MoO₃ powder (2.5 mg) in the corner of the crucible (Figure 5a) to visualize the transition from 2D to 3D MoS₂. An optical image of the grown structure on a Si/SiO₂ substrate is shown in Figure 5b. Variation in the color spectrum of the sample corresponds to different concentrations and morphology of the MoS₂ structures. Detailed morphological characterization was performed by optical and scanning electron microscopy (SEM) as shown in Figure 5c, in which the concentration increases as one moves from left to right. Starting from the low concentration side, initially small triangular MoS₂ monolayer flakes appear on the substrate (Figure 5c-1). As the concentration increases, the flakes grow to larger sizes with some smaller MoS₂ islands growing on top of the flakes (Figure 5c-2). As shown in Figure 5c-3, the flakes keep growing in size, reaching together and making grain boundaries, meanwhile smaller MoS₂ islands begin to grow in the out-of-plane direction on top of the existing flakes. Next, the exiting islands merge together and

eventually form a polycrystalline film with numerous islands of multilayer MoS₂ (Figure c-4). In higher concentration regions (Figure 5c-5), white lines representing thicker MoS₂ structures appear on the polycrystalline film, which are believed to form due to higher local growth rate on the defect sites such as grain boundaries.[76] Moving to even higher concentration regions (Figure 5c-6), the grown structures rapidly convert to 3D granular structures with a high surface roughness and spatial heterogeneity. This abrupt and localized transition from the 2D to 3D structures resembles the Stranski-Krastanov (SK) growth mechanism of thin films, in which the growth mode suddenly changes as the layer thickness exceeds a critical level.[76]–[79] One possible explanation of such sudden transition can be the release of a residual strain induced by thermal and intrinsic stresses between the MoS₂ and the substrate.



Figure 5: (a) Schematic of the MoS_2 CVD setup. (b) Optical image of the grown structure on a Si/SiO₂ substrate. (c) Detailed optical and SEM images of MoS_2 structures shown in b from right to left. (Scale bars in all optical images is 30 µm and in SEM images are 2, 15, 15, 10, 4, 4 µm from left to right, respectively).

To test this hypothesis, we performed Raman spectroscopy on the grown structures from monolayers to 3D structures (Figure 6). Interestingly, we observed that the peak positions of our multilayer films have 3 cm⁻¹ positive shift relative to the bulk spectrum. This shift of spectrum is known to be indicative of an induced strain in the grown structure.[80] However, the peak positions of the 3D structured MoS₂ shift back to the peak positions of the bulk MoS₂, which implies the release of the induced strain. Here, we note that the difference in the positions of the E_{2g} and A_{1g} peaks is known to be dependent on the thickness of the MoS₂ structure[73] which is changing from ~20 cm⁻¹ in single layer to ~25 cm⁻¹ in our multilayer and 3D structures. This is independent of the observed blue shift in the multilayer spectra, which is due to the induced strain.



Figure 6: Raman point spectra obtained from a monolayer flakes (red), multilayer MoS_2 film (blue) and 3D structured MoS_2 (black).

Based on above discussions, we propose a dual-step Stranski-Krastanov mode for the

growth of 3D MoS₂. First, growth initiates from grain boundaries or ordered defects that have high surface energies. Next, the 3D structures form on the film with the thickness beyond the critical point in a less or more compact manner depending on the concentration of Mo and S (Figure 7).



Figure 7: (a) Optical image of multilayer MoS_2 film from the region in which the 3D growth has not yet initiated. (b) SEM image of the region where the 3D growth is just initiated. Line type highly compact patterns of 3D MoS_2 grains similar to the topography of the grain boundaries represents that growth is favorable on the grain boundaries compared with the central parts of the MoS_2 layers (scale bars are 15 µm).

We also synthesized uniform 3D MoS_2 on (i) amorphous glassy carbon (GC), (ii) graphene covered GC and (iii) Si/SiO₂ substrate (transferred to GC for electrochemical experiment). The glassy carbon and graphene substrates are intentionally selected due to their high conductivity, inert nature and wide applicability in various electrochemical systems.[10], [81] For easier characterization, we initially synthesized MoS_2 on partially covered graphene flakes, which was then transferred to Si/SiO₂. Figure 8 and 9 show the SEM and Raman spectra of the 3D structure MoS_2 on graphene film. SEM image illustrates

that the growth is more compact on top of the hexagonally shaped graphene flakes compared to the bare Si/SiO₂. This is attributed to the presence of wrinkles and defects on graphene film which act as nucleation sites and accelerate the growth rate of the 3D structures.[82] This process is also extended to fully covered GC with graphene film for the electrochemical experiments.



Figure 8: SEM image of the 3D structured MoS_2 directly grown on top of partially covered graphene flakes transferred on SiO₂ substrate (scale bar is 20 µm). The insets magnify the 3D MoS₂ in same image as indicated by yellow (bare SiO₂ substrate) and red (on top of graphene flakes) squares.

2.3. Electrochemical experiments and discussion:

Cyclic voltammetry (CV) experiments are then carried out for these catalysts and compared with platinum which is the most efficient catalyst known for HER. All experiments were performed inside the three-electrode electrochemical cell using 0.5 M H₂SO₄ as an electrolyte. Synthesized catalysts, platinum (Pt) gauze 52 mesh (purchased via Alfa Aesar) and Ag/AgCl (3M KCl, purchased from BASi) were used as working, counter and reference electrode, respectively. The reference electrode was calibrated with respect to RHE using platinum mesh for both working and counter electrodes in the same electrolyte ($0.5 \text{ M H}_2\text{SO}_4$) bubbled with pure H₂(99.99%). The calibration results in 0.164 V shift versus RHE. All CV experiments were obtained by sweeping potential between +0.1 to -0.7 V vs RHE with the scan rate of 5 mV.s⁻¹ using a CHI-600D potentiostat. The current densities are normalized with respect to the geometrical surface area and reported based on RHE (reversible hydrogen electrode) scale. As shown in Figure 9, both MoS₂ on SiO₂ (transferred to GC) and directly grown on GC exhibit low onset potentials of 175 and 140 mV, respectively. Interestingly, the HER takes place at a much smaller onset potential (70 mV vs RHE) for the MoS₂ on graphene sample. In particular, 10 mA.cm⁻¹ current density is achieved at ~100 mV overpotential. A similar HER current density was recorded at ~180 mV overpotential for the recently studied efficient thiomolybdate clusters.[9]



Figure 9: Cyclic voltammetry curve for Platinum, MoS₂ grown on graphene, grown on GC and Transferred to GC.

Additionally, the linear part of Tafel plot for three different catalysts was studied to further explore their catalytic properties and HER mechanisms.^{5,17} In general, three

elementary reaction steps that can control the rate of HER are: (i) adsorption of reactant (H⁺) on catalyst active sites (Volmer step), (ii) intermediate formation (H_{ad}, Tafel step), and (iii) product desorption (Heyrovsky step) from active sites.^{25–27}

$$H^{+} + e^{-} \rightarrow H_{ad}$$
 (Volmer, rxn 1)

$$H_{ad} + H_{ad} \rightarrow H_{2}$$
 (Tafel, rxn 2)

$$H^{+} + e^{-} + H_{ad} \rightarrow H_{2}$$
 (Heyrovsky, rxn 3)

Tafel slops of 120, 40, and 30 mV.dec⁻¹ are correlated to Volmer, Heyrovsky and Tafel step, respectively, as a rate determining step (RDS) for HER.²⁷ The obtained Tafel slope and exchange current density for different studied catalysts are shown in Figure 10a-b and Table 1. The Tafel slop for MoS₂ on graphene is ~41 mV.dec⁻¹ proposing the Volmer-Heyrovsky (rxn 1 and 2) as a dominant mechanism and Heyrovsky step as a RDS.[9], [10], [83]–[85] Tafel slop for MoS₂ on GC (~55 mV.dec⁻¹) and transferred MoS₂ (~68 mV.dec⁻¹) also suggest similar mechanism with Heyrovsky step as a RDS. However, the calculated lower Tafel slope (~41 mV.dec⁻¹) and higher exchange current density (18.2 μ A.cm⁻²) for the MoS₂ on graphene (Table 1) implies a remarkable improvement in the charge carrier mobility of the MoS₂.


Figure 10: (a) Tafel plot obtained for different catalysts. 3D MoS₂ grown on graphene shows lower Tafel slop than that of grown on GC or grown on Si/SiO₂ and transferred on GC. (b) Extrapolation line to measure exchange current density (A.cm⁻²) of MoS₂ grown on graphene, grown on GC and transferred to GC compared with Pt at zero over potential.

Table 1. Extracted exchange current density of MoS_2 grown on graphene, MoS_2 grown on GC and MoS_2 transferred to GC compared with Pt

Catalyst	Intercept at η = 0	Exchange current density (A.cm ⁻²)
MoS ₂ grown on graphene	-4.74	1.82×10^{-5}
MoS ₂ grown on GC	-4.95	1.12×10^{-5}
MoS ₂ transferred to GC	-5.92	$1.2 imes 10^{-6}$

To further explore the reaction mechanism and effect of graphene in catalytic performance of MoS₂, we performed binding energy measurement in 0.1M perchloric acid (HClO₄) solution at potential ranging from -0.1 to 0.4 V vs Ag/AgCl with the scan rate of 10 mV.s⁻¹ (Figure 11). In principal, a lower over-potential corresponds to a higher binding energy at the constant current density.[23], [86] The binding energy measurement shows strong adsorption (lower over-potential) for Pt compared to MoS₂ on graphene suggesting intermediate formations (Tafel step) as a RDS. This is consistent with Tafel slope of 33

mV.dec⁻¹ measured for Pt (Figure 11). However the desorption peak shows opposite trend where MoS_2 on graphene exhibits higher desorption energy compared to Pt and MoS_2 on GC. This further verifies the Heyrovsky step as a RDS where desorption of the produced species from the catalyst surface is known to be the rate determining step for the reaction.[9], [10], [83]–[85] Furthermore, the binding energy experiment shows strong adsorption and desorption (lower over-potential) for MoS_2 in presence of graphene. We attribute this to an enhanced contact resistance between graphene and $MoS_2[85]$, [87], [88] which could boost electrons transfer toward active edge sites.



Figure 11: Binding energy measurement for Pt, MoS_2 on graphene and GC in 0.1M HClO₄ solution. The results confirm higher adsorption and desorption energy for MoS_2 on graphene at the constant current density compared to direct grown MoS_2 on GC.

We also performed electrochemical impedance spectroscopy (EIS) experiments to study the charge transfer resistances (R_{ct}) in the MoS₂ catalyst with and without the graphene layer. The Nyquist plots were recorded at overpotential of 150 mV to ensure that the HER takes place on both catalysts (Figure 12a). An equivalent Randles circuit model

was applied to calculate R_{ct} value for each system (inset of Figure 12-a). The MoS₂ on graphene exhibits much smaller R_{ct} (~65 Ω) compared to that of without graphene layers (>150 Ω).



Figure 12: Nyquist plots collected from EIS experiments at overpotential of 150 mV for 3D MoS_2 grown on graphene and GC, evidencing higher charge transfer rate for 3D MoS_2 grown on graphene. An equivalent Randles circuit was fitted to the data to calculate R_{ct} value for each catalyst system (inset).

Figures 13a and b also show the EIS results for the MoS₂ on graphene and GC during HER at different over-potentials. Results indicate a smaller charge transfer resistance[10], [89] at all over-potentials due to enhanced contact between MoS₂ and graphene further supporting the results of binding energy measurements.



Figure 13: EIS results for MoS₂ grown on (a) graphene covered GC, (b) GC substrate at different over-potentials. The Recorded Nyquist plot clearly shows the low charge transfer resistance (Rct) of MoS₂ grown on graphene catalyst at all over-potentials resulting in a much faster electron transfer during HER.

The turnover frequency is also calculated (TOF) for different MoS₂ catalysts using the roughness factor (RF) method[7]. The RF number of our catalyst is determined by comparing the double layer capacitor (C_{dl}) of this catalyst with flat standard MoS₂ (60 μ F.cm⁻¹). The CV experiment at different scan rates was used to calculate the C_{dl} of catalysts[4] (Figure 14a). The extracted C_{dl} values from the slope of current density-scan rate graphs at +0.2 V (Figure 14b) are equal to 2.13 and 1.68 mF.cm⁻¹ for MoS₂ on graphene and GC, respectively. The calculated number of active sites for MoS₂ on graphene (4.07×10¹⁶ sites.cm⁻²) is ~ 1.2 times higher than those of amorphous GC (3.21×10¹⁶ sites.cm⁻², equation 1).

Density of active sites for catalyst (Sites/cm²) = Density of active sites for standard sample× RF (equation 1)

Moreover, the calculated TOFs (equation 2) for MoS₂ on graphene show higher values at entire range of overpotentials (Figure 14c and Figure 14d).

$TOF(s^{-1}) = i_0(A/cm^2) / \{ [active sites density(sites/cm^2)] \times [1.602 \times 10^{-19} (C/e^{-})] \times [2e^{-10} / H_2] \} (equation 2)$

In particular, TOF at 200 mV overpotential is > 4 (s⁻¹) which suggest a remarkable activity of the catalyst for HER. The extended TOFs calculated at higher over-potentials (>200 mV) is also presented in the Figure S14d.



Figure 14: Electrochemical measurement for determining TOF: (a) a cyclic voltammetry (CV) curve of MoS_2 grown on graphene at different scan rates. (b) Current density of CV experiment at overpotential +0.2 V vs RHE as a function of scan rates. The slope of this line shows double layer capacitor for MoS_2 grown on graphene catalyst system (2.13 mF.cm⁻²). (c) Calculated TOF at different current densities with respect to the overpotentials smaller than 200 mV. (d) The extended TOF with respect to the over-potentials (> 200 mV) and different current densities.

The stability of the MoS₂/ graphene catalyst was studied during 1000 continues cycles of CV experiment (Figure 15). The cycles were performed between 0.1 V and -0.2 V with 100 mV.s⁻¹ scan rate. The magnetic stirring system and continuously bubbling of pure H₂ (99.99%) inside the solution were applied to eliminate mass transfer effect during the stability experiment. As shown in Figure 15, after 1000 cycles CV experiment the cathodic current density changed by <2 mA.cm⁻², at the same overpotential (0.15 mV) which confirms high stability of our MoS₂/ graphene catalyst during HER.



Figure 15: Stability of MoS_2 grown on graphene after 1000 continues CV cycles. This catalyst shows negligible shift (< 5%) of current densities for increased potential cycling.

2.4. Density functional theory (DFT) calculation:

Density functional theory (DFT) calculations were carried out to investigate the catalytic properties of the bare Mo edge of MoS_2 and the support effect of graphene. The unsupported MoS_2 nanoribbon was calculated to represent MoS_2 transferred onto the glassy carbon in the experiment, due to the weak effect from the support. The MoS_2

nanoribbon supported on graphene was calculated to represent MoS₂ on graphene. We studied the relationship between the theoretical MoS₂ hydrogen binding energy and the experimental HER exchange current density (Figure 16). Previous studies of HER on pure metal surfaces[90] have suggested that the experimental exchange current density is directly correlated with the adsorption free energy of hydrogen (Figure 16). Too strong/weak hydrogen binding leads to a low activity of HER, while a material with the hydrogen adsorption energy close to 0 gives the highest activity, i.e., Pt surface. We noticed that the Mo terminated MoS₂ system shows a similar relationship between hydrogen binding energy and activity. Both unsupported MoS_2 and MoS_2 on graphene show negative hydrogen adsorption energies. This indicates that formation of the adsorbed hydrogen, H_{ad}, is thermodynamically downhill (the Volmer step), while the second step of HER, the formation of H₂, is the RDS. Thus, given the reaction follows the Volmer-Heyrovsky mechanism for the MoS_2 systems, the calculated hydrogen adsorption energies confirms the experimental results that the Heyrovsky step is the RDS. The hydrogen desorption on MoS_2 on graphene became slightly weaker than that on the unsupported MoS_2 . The slightly weaker hydrogen binding energy induces a remarkable change in the exchange current density as well as the TOF of HER (Figure 16). It is notable that the measured exchange current density of the bare Mo edge of MoS₂ on graphene is higher than the previously reported MoS_2 /graphene and MoS_2 /Au(111), in both of which the Mo edges were sulfided. This suggests that the MoS_2 with bare Mo edge synthesized in this study has unique catalytic properties, compared to previously studied systems.



Figure 16: Activity relationship for the hydrogen evolution reaction (HER) showing the exchange current density as a function of the calculated free energy of hydrogen adsorption, ΔG_H . The black points are experimental data of exchange current density and computational ΔG_H [90]. The blue points represent measured rates on sulfided Mo edge of MoS₂ nanoparticles on either Au(111)[5] or graphene[91] plotted at the calculated ΔG_H [92]. The red points are the experimental data and the calculated ΔG_H from this study, in which the ΔG_H of bare Mo edge of MoS₂ (without a support) was calculated to represent the MoS₂ transferred onto glassy carbon, due to the weak interactions between MoS₂ and the support. It was assumed that surfaces with negative ΔG_H have high coverage ($\theta_H = 1$ ML) and surfaces with positive ΔG_H have low coverage ($\theta_H = 0.25$ ML), where θ_H is defined as the fraction of a monolayer with respect to the number of edge metal atoms[91], [92]. Thus in this study we use the same assumptions for the coverages.

2.5. Summary and Conclusion:

In conclusion, using CVD method, we synthesized 3D structured MoS_2 with Mo edge atoms and with high degree of crystallinity on the graphene film with the aim of enhancing the HER performance. The observed improvement is mainly attributed to high number of active edge sites of 3D structured MoS_2 , enhanced charge transfer toward active edge atoms and optimized hydrogen binding energy due to the presence of graphene. The ability to directly grow these 3D structures over a wide range of substrates enables ready assimilation of these new materials in any arbitrary platform for various energy conversion and storage technologies.

3. CHAPTER 3: CO₂ reduction reactions

Theoretical and experimental studies of CO_2 reduction reveal that following processes occur to complete this reaction: (i) diffusion of reactants (i.e., CO_2 and H^+) from bulk electrolyte into the double layer where the electrons are transferred to the reactants, (ii) conversion of CO_2 to high energy species i.e., CO_2^- due to one electron transfer process, (iii) interaction between formed CO_2^- and H⁺ and formation of products (i.e., CO and H₂), and (iv) diffusion of formed products from the double layer back to the bulk electrolyte[93]. Thermodynamically, the conversion of CO_2 to CO_2^- is an energy consuming process (-1.9 V)[13], [24], [93], [94], and this step is known to be the rate determining step for CO_2 reduction in most cases. This process has always required applying large electrical voltages for CO₂. That excess voltage is an energy loss, meaning that the conversion process requires far more energy to create a useful product than what can be stored in its chemical bonds. Add to this, in aqueous electrolytes, CO₂ reduction competes with the hydrogen evolution reaction (HER)[95]–[99] which is thermodynamically favored over the reduction of CO_2 . Therefore, new advanced materials with unique catalytic feature (i.e., activity and selectivity) are essential to boost the energy activity and efficiency of this process.

3.1. Bulk MoS₂ for CO₂ reduction

3.1.1. Introduction

During the last few decades, the amount of carbon dioxide (CO₂) present in the environment has reached the highest level (396.80 ppm) of the last 20 million years[100], causing radical and largely unpredictable changes in the environment[11], [12], [101]. Recent efforts have revealed that CO₂ can be converted by electrochemical reduction processes using renewable energy sources into energy-rich modules, offering an efficient path for both CO₂ remediation and an alternative energy source[23], [24], [26], [28], [102]. However the CO₂ reduction by electrochemical processes faces various fundamental and practical challenges mainly due to high-cost and unsatisfactory conversion performance of existing catalytic systems[28]. Numerous physical and chemical approaches have been employed to improve the performance of existing CO₂ reduction systems[13], [25], [94], [103] without achieving a major breakthrough.

Recently, molybdenum disulfide (MoS_2) and related layered materials have attracted a significant attention due to their low price and prominent catalytic features. MoS_2 became widely used as an efficient catalyst for hydrodesulphurization[5], [104], oxygen reduction reactions[105], and hydrogen evolution reaction (HER)[5], [105]. Moreover, it was demonstrated that MoS_2 has a noteworthy performance for water splitting, approaching that of Pt-group metal[105]–[107].

In this study, we found that layer stacked bulk MoS₂ with molybdenum (Mo) terminated edges exhibits the highest CO₂ reduction performance reported yet. This performance was shown in a diluted solution of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) ionic liquid *i.e.* 4 mol% EMIM-BF₄ and 96 mol% water. EMIM-BF₄ was purposely chosen due to its' particular catalytic features which make the system more selective for CO formation rather than hydrogen (H₂) production[23], [24], [26]. In the same diluted electrolyte, commonly used silver nanoparticles (Ag NPs) exhibit moderate performance while a bulk silver (Ag) catalyst is unable to reduce CO₂. The high catalytic activity of bulk MoS₂ is attributed to the Mo terminated edges, where the Mo atoms possess approximately one order of magnitude higher (d orbital) electronic density than Ag atoms at the surface of an Ag film, as shown by our first principle calculations. The lower work function (3.9 eV) also promotes the advanced performance of the MoS₂ catalyst[108]. The performance of the MoS₂ catalyst is further improved by designing an atomic edge terminated surface via synthesizing vertically aligned MoS₂.

3.1.2. characterization

Figure 17a-b shows optical and scanning electron microscopy (SEM) images, respectively, of the layered structure[109], [110] of our bulk MoS₂ sample. Such layered assemblies offer a large number of edges (inset of Fig. 1b), which are believed to be highly electrocatalytically active sites in electrochemical reactions[91], [105]. To further detail the atomic arrangement, scanning transmission electron microscopy (STEM) analysis was performed on several mechanically exfoliated, mono- and multi-layer thick sheets of MoS₂ flakes. Since the STEM high-angle annular dark-field (HAADF) image intensity relies on the atomic number (Z), it delivers direct information about the arrangement of Mo and S atoms in the MoS₂ film. The results of the STEM structural (Fig. 17c) and Fast Fourier transform (FFT) analyses show that the MoS₂ layers are made of two clearly distinct structural domains consisting of 1T (octahedral) and 2H (triangular prismatic). The magnified images (atomic resolution) of selected regions confirm the co-existence of both 1T and 2H atomic arrangements (Fig. 17d).



Figure 17: Structural and elemental analysis of MoS₂, (a) Optical image of bulk MoS₂ used as catalyst (scale bar, 2 mm), (b) SEM images of the MoS₂ displaying the stacked layered structure and sharp edges of the MoS₂ flakes. Scale bars are 50 and 5 μ m (for inset) respectively, and (c) high-angle annular dark-field (HAADF) images (scale bar, 5 nm) showing both the 1T (blue) and 2H (red) phases of MoS₂, along with their respective Fast

Fourier Transforms (FFTs) (inset). (d) Higher magnification HAADF images show clearly distinct atomic configuration corresponding to the 1T (top) and 2H (bottom) type of MoS₂. The related schematic atomic models have also been shown on the right side. (e) Raw grayscale HAADF and false-color low-angle annular dark-field (LAADF) image (inset) of MoS₂ edges (scale bar, 5 nm) and (f) the line scans (red and blue towards edges) identifying Mo atoms to be the terminating atoms in the general case. In limited instances, an additional light atom (gray line scan) occupying what should be a Mo-position, most probably a carbon atom from the STEM substrate. Identification of the atoms on the MoS₂ edges is also crucially important, as the Mo and S

atoms possess entirely different electronic structures. Figure 17e shows the edge of a MoS₂ flake imaged in HAADF and low-angle annular dark-field (LAADF) (inset) mode. The line intensity profiles (plotted towards vacuum) suggest that the edges of the MoS₂ flakes are Mo terminated (Fig. 17f). This finding is in agreement with the earlier work by Zhou *et. al.*[45] who report that the Mo-terminated edges have the lowest formation energy in free-standing single layer MoS₂. In rare instances, a substitutional defect (atom) appears at the MoS₂ edge. Based on the LAADF image (inset of Fig. 17e) and the line intensity profile (gray line), it is clear that this is a lighter atom (compared to S), most likely a carbon atom (from the underlying holey carbon STEM grid). Hence, the STEM analysis undoubtedly validates the presence of Mo atoms on the edges of MoS₂ flakes.

3.1.3. Catalytic evolution:

3.1.3.1. Electrochemical experiments

The CO_2 reduction ability of bulk MoS_2 covered by flakes with exposed Mo-ended edges was first examined by performing a cyclic voltammetry (CV). All electrochemical experiments were carried out in a custom made 2-compartment three-electrode

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electrochemical cell (Figure 18). The compartments were separated by a physical barrier using glass frit. Bulk MoS₂ (purchased through SPI Supplies), platinum (Pt) gauze 52 mesh (purchased via Alfa Aesar) and Ag wire (annealed 99.9% metal basis, purchased from Alfa Aesar) were used as working, counter and reference electrode respectively. 1-ethyl-3methylimidazolium tetrafluoroborate (EMIM-BF₄) was purchased through Sigma-Aldrich. Electrolytes with different water mole fractions were prepared by adding known volume of DI water into EMIM-BF₄. Electrochemical CO₂ reduction experiments were performed in anaerobic CO₂ (AirGas) saturated electrolyte. The applied voltage was swept between +1.0 and -0.764 V vs. RHE (reversible hydrogen electrode) with a 15 mV/s scan rate. Cyclic voltammetry (CV) curve was then recorded using a Voltalab PGZ100 potentiostat (purchased via Radiometer Analytical SAS) calibrated with a RCB200 resistor capacitor box. The potentiostat was connected to a PC using Volta Master (version 4) software. For chrono-Amperometry (CA) measurement, CO₂ concentration was kept constant with bubbling high purity CO₂ in solution along with mixing during experiment. Current densities were normalized with catalyst geometrical surface area[5], [85], [94], [105], [111].



Figure 18: Optical image of 2-compartment three-electrode electrochemical cell. The working electrode (WE), counter electrode (CE) and the reference electrode (RE) are immerged in the ionic liquid solution (EMIM-BF₄) and connected to the potentiostat for electrolysis characterization. Silver wire and platinum net were used as RE and CE respectively. A 6 mm dia polyethylene tube is used for bubbling the gas (Argon or CO_2) into the solution for required time.

3.1.3.2. Product analysis

Electrochemical experimental yields were analyzed by gas chromatography (GC) in SRI 8610C GC system equipped with $72 \times 1/8$ inch S.S. molecular sieve packed column and a Thermal Conductivity Detector (TCD). Production of carbon monoxide (CO) and hydrogen (H₂) was examined separately. Ultra High Purity (UHP) Helium (purchased through AirGas) was used as a carrier gas for CO detection whereas UHP Nitrogen (Air Gas) was utilized for H₂ detection. Initially, GC system was calibrated for CO and H₂. A

JEOL GCMate II (JEOL USA, Peabody MA) gas chromatograph/mass spectrometer was further used to prove that yielded CO is only CO₂ electrochemical reduction product. The gas chromatograph was an Agilent 6890Plus (Wilmington DE) equipped with a G1513A auto-injector with 100 vial sample tray connected to a G1512A controller. The gas chromatography column was a fused silica capillary column with a nonpolar 5% phenyl 95% dimethylpolysiloxane phase (Agilent HP-5ms Ultra Inert), 30 meters long, 0.25 mm internal diameter, 0.25 um film thickness.

Figure 19a represents the CV curve for the CO₂ reduction. It should be noted that the CO₂ reduction equilibrium potential is -0.11 V vs. RHE in the protic media[24], [94]. We observed that CO₂ reduction reaction initiates at -0.164 V confirmed by measuring CO as a product by gas chromatography (GC) system (CO Faradaic efficiency F.E. = \sim 3%). This suggests a very low overpotential (54 mV) for CO formation in our system. At -0.2 V (90 mV overpotential) approximately 7% CO formation F.E. was measured (Fig. 19b). MoS₂ also exhibits a significantly high CO₂ reduction current density (65 mA/cm² at -0.764 V), where CO₂ is selectively converted to CO (F.E. \sim 98%).



Figure 19: CO₂ reduction performance of the bulk MoS₂ catalyst in the EMIM-BF₄ solution: (a) Cyclic voltammetric (CV) curves for bulk MoS₂, Ag nanoparticles (Ag NPs) and bulk Ag in CO₂ environment. The experiments were performed in 96 mol% water and 4 mol% EMIM-BF₄ solution by sweeping applied potential from +1 V to -0.764 V vs RHE. The vertical gray line indicates the low overpotential (~54 mV) for CO₂ reduction at bulk MoS₂. (b) CO and H₂ Faradaic Efficiency (F.E) at different applied potentials.

However, at the same potential (-0.764 V) the bulk Ag catalyst shows a considerably lower current density (3 mA/cm²) (Fig. 19a) but for the H₂ formation (Figure. 20a). Ag NPs (average diameter of 40 nm) show only a current density of 10 mA/cm² with 65% selectivity for the CO formation under the same experimental conditions (Figure. 19a and Figure. 20b).



Figure 20: Faradic efficiency (F.E.) measurement for Ag nanoparticles (Ag NPs) and bulk Ag. Ag nanoparticles and bulk Ag CO₂ reduction performance was examined in 4mol% EMIM-BF₄ solution in DI water at different potentials. (a) CO and H₂ formation Faradic Efficiency (F.E.) for bulk Ag and (b) Ag nanoparticles (Ag NPs). At the highest applied potential, the CO formation F.E. remains only 65% for Ag NPs while bulk Ag is unable to reduce CO₂ at any applied potential under these experimental conditions (4mol% EMIM-BF₄ solution).

In addition, the CO₂ reduction current density for MoS₂ is also significantly higher than the maximum current density (~8.0 mA/cm²) achieved when Ag NPs were used in the dynamic electrochemical flow cell using a similar electrolyte solution[25]. For all the cases, the current densities were normalized against the geometrical surface area[5], [13], [24], [25], [94], [111]. Surprisingly, the MoS₂ catalyst also shows a high current density (50 mA/cm²) in an Ar-saturated electrolyte, where only H₂ was detected as the major product (Figure. 21). To find a normalized current density in a saturated CO₂ environment, we run first an experiment with a fully argon (Ar) saturated solution in 96 mol% water and 4 mol% ionic liquid (EMIM-BF₄) and compared the current density, products, and faradaic efficiencies attained in CO₂ saturated solution. Surprisingly, we observed high current density (50 mA/cm2) in Ar saturated environment (Figure. 21). Analyzing product by gas chromatography (GC) showed 100% F.E. of H₂ in saturated argon-saturated solution at a potential of -0.764 V vs. RHE. This evidences that bulk MoS₂ has a high catalytic activity towards hydrogen evolution reactions (HER) in the presence of 96 mol% water and 4 mol% ionic liquid (EMIM-BF₄) solution as electrolyte. It should be noticed that HER proceeds either by the Volmer-Tafel or Volmer-Heyrovsky mechanism[85], [112], [113]. Firstly, H⁺ adsorbs on the catalyst surface and associates with electrons (Volmer step). Subsequently, two adsorbed hydrogen atoms on the catalytic surface may fuse into a hydrogen (H_2) molecule (Tafel step). Alternatively, H^+ may directly react with a hydrogen atom and an electron on the surface resulting in the production of H2 molecules (Heyrovsky step). Recent reports suggest that Volmer-Heyrovsky mechanism leads over Volmer-Tafel mechanism for a bulk MoS2 catalyzed HER[112], [113]. Based on STEM results and DFT calculations, Mo terminated edges seem to have a large number of electrons available for the reaction. In diluted electrolyte (low pH-3.98) the system also carries excess of H^+ . Therefore, in favorable conditions (i.e. excess of electron and H^+), we observe a high current density for HER.



Figure 21: Catalytic performance of bulk MoS_2 catalyst in Argon (Ar) environment: Cyclic voltammetric (CV) curves of bulk MoS_2 catalyst in the 96 mol% water and 4 mol% EMIM-BF₄ solution and ultra-high purity Ar environment. Only hydrogen (H₂) was identified as product.

Figure 19b also shows the measured F.E. of the CO and H₂ formation for a wide range of applied potentials between -0.2 and -0.764 V. Interestingly, depending on the applied potential, MoS₂ effectively operates as a catalyst for both CO₂ reduction and HER. CO₂ is converted at MoS₂ into a tunable mixture of H₂ and CO (syngas), ranging in each component from zero to ~100%. The variation in F.E. of CO and H₂ as a function of the applied potential originates from the differences in the CO₂ and HER reduction mechanisms. In principle, the favorable thermodynamic potential for the H₂ evolution is lower than CO₂ reduction. As the applied potential exceeds the onset potential of the CO₂ reduction (-0.164 V), this reaction is activated. Essentially, two H⁺ are consumed for a CO formation as a result of one CO₂ molecule reduction[24], [25], [94], [95], [98]. Thus, a fraction of both the existing H⁺ (from the electrolyte) and the electrons (on the catalyst

surface) are consumed in CO_2 reduction reactions instead of HER reactions. In addition, the EMIM-CO₂ complex works as an inhibitor for the H₂ formation in HER[24].

In order to confirm that the CO product is derived from CO₂, an isotope ¹³CO₂ was used as feedstock and GC-Mass spectroscopy was used for gas detection. Mass spectrometer was a bench top magnetic sector operating at a nominal resolving power of 500 using an accelerating voltage of 2500 volts. The spectrometer was operated in full scan EI mode (+Ve) with the filament operating at 70 eV scanning from m/z 10 to m/z 400 using a linear magnet scan. The scan speed was 0.2 sec per scan. Data analysis was performed using the TSSPro software (Shrader Analytical & Consulting Laboratories, Inc., Detroit MI) provided with the spectrometer. Mass calibration was performed using perflourokerosene (PFK).The results are discussed in supplementary file (Figure 22).



Figure 22: Gas Chromatography/Mass spectroscopy of 2 mL gas sample extracted from sealed three-electrode electrochemical cell. m/z stands for mass-to-charge ratio. (a) Raw sample data which is injected to GC-Mass spectroscopy for gas detection, (b) Back ground gas data (c) Deconvoluted data which is derived from subtracting raw sample data from background data.

Here, it is useful to compare the MoS_2 catalyst performance with the existing results for noble metal catalysts (Figure. 23). It should be noted that current density represents the CO formation rate, whereas F.E. shows the amount of current density consumed to produce CO during the CO₂ reduction reaction. Thus, we compared the catalysts' overall performance by multiplying these two parameters at different overpotentials. Interestingly, we noticed that bulk MoS₂ exhibits the highest performance at all overpotentials. At low overpotentials (0.1 V), bulk MoS₂ shows almost 25 times higher CO₂ reduction performance compared to the Au NPs[94] and ~1.3 times higher than the Ag NPs. At higher overpotentials (0.4 V), bulk MoS₂ exhibits approximately one order of magnitude higher performance than Ag NPs and more than two times higher than recently reported nanoporous Ag (np Ag)[114]. At this overpotential the Au NPs compete with bulk MoS₂. It should be noted that MoS₂ produce H₂ as a by-product which allows obtaining directly synthetic-gas while Au NPs produces formic acid (HCOO⁻) as a by-product in the examined conditions[94]. As mentioned previously, bulk Ag is unable to reduce CO₂ in the examined experimental conditions. Moreover, the Cu performance[13] remains below that of Ag NPs, Au NPs and bulk MoS₂. These results clearly indicate that MoS₂ exhibits the highest CO₂ reduction performance reported so far.



Figure 23: Overview of different catalysts' performance at different overpotentials (η). Bulk MoS₂, Ag nanoparticles (Ag NPs) and Bulk Ag results were taken from the present study where electrochemical experiments were performed in similar conditions. Oxidized Au nanoparticles (Au NPs) and polycrystalline Au (PC Au) data were carefully extracted from the reference ([94]). Annealed copper (Anld Cu) and polycrystalline Cu (PC Cu) data were taken from reference ([13]). Nano porous Ag (np Ag) data were extracted from reference ([114]). CO₂ reduction performance curve of bulk Ag is not visible as it is unable to reduce CO₂ in experimental conditions discussed in the text. The extended results are provided in the supporting file.

Next, we investigated how the water mole fraction affects the catalytic activity of the MoS_2 catalyst for the CO_2 reduction (Figure. 24a). We observe that the CO_2 reduction current density largely grows above 90 mol% water solution densities (inset Figure. 24a) and reaches a maximum in the 96 mol% water solution. The addition of water molecules can tailor the pH value (i.e. H⁺ concentration) of the [25], [115], [116] (Table 2) and consequently affect the electrochemical reduction reaction rate. The pH of the electrolyte fluctuates due to the hydrolysis of BF_4^- , which produces anions [e.g. (BF_3OH)⁻] and [25], [115], [116]

Water mole fraction	рН
0 mol% H ₂ O	6.54
10 mol% H ₂ O	4.98
25 mol% H ₂ O	4.87
50 mol% H ₂ O	4.54
94 mol% H2O	3.78
96 mol% H2O	3.98
98 mol% H ₂ O	4.82
99 mol% H ₂ O	5.30
99.5 mol% H ₂ O	5.98

Table 2: pH value with respect to water mole fraction (measured by pH meter)

It should be noted that the overall CO₂-to-CO conversion reaction requires both electrons and protons[25]. Our DFT calculations show significantly higher density (more than one order of magnitude) of d-electrons on Mo-edge atoms compared to Ag (for details see section 3.4.), suggesting that the concentration of protons (H⁺) is the rate-determining part of the CO₂ reduction reaction. Thus, the attained maximum rate of the reduction process is attributed to: (i) the high concentration of H⁺ (pH ~4) in the reaction media and (ii) the low viscosity of the solution. It is clear that the low viscosity allows for a high diffusion rate of the reactants (EMIM-CO₂⁻ and H⁺) towards the catalyst's active edge sites[117]– [119]. A similar trend was observed for Ag NPs catalysts in a dynamic electrochemical flow cell when the maximum current density (~8 mA/cm²) was obtained in a 90 mol% water electrolyte[25]. Additionally, a catalyst's stability is a major issue to be addressed. Thus, we examined the stability of the catalyst for a prolonged period (10 hrs) in 96 mol%, 90 mol% and 0 mol% water solutions. As seen in Figure 24b the steady state current densities remain stable for the studied time (10 hrs), providing evidence of the long term stability and efficiency of the MoS₂ catalyst.



Figure 24: (a) The current density of CO_2 reduction (measured by Chrono-Amperometry) at -0.764 V vs. RHE as a function of water mole fraction in 4 mol% EMIM-BF₄ electrolyte. The pH value of the solutions was also monitored (SI file). (b) Chrono-Amperometry results of MoS₂ catalyst in different solutions (96 mol%, 90 mol% and 0 mol% water) showing negligible loss in current density even after 10 hours.

3.1.4. Mechanistic study and discussion

In order to elucidate the origin of the high CO_2 reduction rate on the MoS_2 catalyst, we calculated its projected electron density (PDOS) per different Mo and S atoms[108], [120], [121], using density functional theory (DFT) methods (for computational details see method section). The density of states (DOS) at the Fermi energy level (E_f) roughly determines the availability of electrons for a given reaction[120]. We found that the

electronic structure of MoS_2 ribbons is near E_f formed by edge bands of only one spin polarization, originating from the Mo and S atoms exposed at both MoS_2 edges. In the vicinity of E_f , the spin-polarized PDOS for these Mo atoms is approximately twice larger than that of the bulk Mo atoms (Figure. 24a). Since the bulk Mo atoms, sandwiched between two S layers, are not directly exposed to the electrolyte, the MoS_2 catalytic activity should be primarily related to the edge states formed by Mo-edge atoms.



Figure 25: DFT calculations of electron density. Projected density of states (PDOS) for spin up channel of: (**a**) the Mo atom at the edge and Mo atom within the lattice; (**b**) s, p, and d orbital of Mo-edge atom. (**c**) PDOS of d-band of Mo-edge atom, Ag atom from bulk and Ag-slab of 8.32 Å thickness. Electron density on Mo-edge atom is significantly (~11 times) higher than the electron density on Ag atom.

The S atoms possess less reactive p-orbitals (Figure. 25), and they are not present at the catalytically active edge sites (confirmed by STEM).



Figure 26: Projected Density of State (PDOS) for spin up channel of the edge sulfur (S) atoms in single MoS₂-nanoribbon: Contributions of s-, p-, and d-orbitals to DOS of the edge S atoms are shown. DOS of the edge S-atoms at the Fermi level is mostly due to p- atomic states, which are not expected to be electrochemically active in the CO₂ reduction.

Next, we resolved the PDOS of the Mo-edge atoms into s, p and d-orbital electron contributions (Figure. 24b). The obtained data indicate that near E_f the PDOS is dominated by d-orbital (Mo) electron states, which are known to actively participate in catalyzed reactions[120]. The Mo d-electrons form metallic edge states[122], which can freely supply electrons to the reactants attached at the edges. To assess how the Mo-edge states are affected by the presence of additional MoS₂ layers, we performed the same analysis for a double-layer MoS₂ strip. Our calculations showed that an interlayer coupling further increases the d-electron PDOS near E_f . In the presence of an external bias all these d-electron states near E_f can be accessed in the reaction, supporting the large observed MoS₂

activity. Finally, we compared our d-orbital PDOS in Mo-edge atoms to that in Ag atoms in two structures: a bulk Ag and a two-dimensional slab Ag (both fcc lattice with a lattice constant of 4.09 Å) of a 8.32 Å thickness (after relaxation) (Figure. 24c). We found that the d-band center for Mo edge atoms is closer to the Fermi energy level than that in both Ag structures. This can partly explain the high catalytic activity of MoS_2 , since the higher the d-band center is, the more reactive the metal is due to a lower transition state energy[120]. Moreover, the PDOS of Mo-edge atoms near E_f is approximately one order of magnitude higher than the PDOS of Ag atoms, suggesting the availability of the excess of d-electrons on the Mo-edge atoms. We believe that both these factors are mainly responsible for the high CO₂ reduction current density of MoS₂.

In order to reveal the role of EMIM ions in carrying CO₂ molecules, we have also performed quantum molecular dynamics (QM/MM) simulations (TeraChem) of the [EMIM-CO₂]⁺ complex hydrated in quantum water. We have tested the effect of different pH of the solution on the [EMIM-CO₂]⁺ complex stability in several possible configurations. Our simulations reveal that CO₂ most likely binds to EMIM⁺ through the C4/5 protons than through the C2 proton (known to provide stronger binding in vacuum). In this configuration the complex appears more stable (bond length) and it also provides a better protection against the conversion of CO₂ into HCO₃⁻ and CO₃²⁻ species.

Our simulations revealed that the EMIM⁺ cation forms a complex $[EMIM-CO_2]^+$ with CO₂ stabilized by hydrogen bonding (Figure 26). However, the complex form depends on the pH of the electrolyte. In neutral solution, within ~2 ps, the $[EMIM-CO_2]^+$ complex reacts

with water molecule, forming either the [EMIM-HCO₃] or [EMIM-CO₃]⁻ complexes (Figure 26a). It is well known^{Error! Reference source not found.} that in neutral and basic conditions CO_3^- and CO_3^{2-} are the dominant species, respectively. However, our QM/MM simulations reveal that in acidic environment, similar to our experimental conditions (pH<4), the [EMIM-CO₂]⁺ complex remains stable (Figure 26).



Figure 27: Formation and stability of [EMIM-CO₂]⁺ complex. First row (complex near the C₄ proton): (a) Formation of the [EMIM-HCO₃] complex in neutral conditions. (b) Formation of the [EMIM-CO₂] complex in acidic conditions. (c) Time dependence of the hydrogen bond length formed between CO₂ and EMIM⁺. Second row (complex near the C₂ proton in acidic pH): (d) Initial configuration [EMIM-CO₂] complex with the H-bonds shown between the C₂ proton (highlighted by iceblue) and the oxygen (highlighted by orange) from CO₂. (e) Stabilization of the [EMIM-CO₂] complex with an additional coordination of CO₂ and a water molecule (the oxygen is highlighted by orange). (f) Time dependence of the hydrogen bond length between CO₂ and EMIM⁺ and between CO₂ and an adjacent water molecule.

These results agree with our previous in-situ EMIM-CO₂ complex formation studies[121]. The [EMIM-CO₂]⁺ complexes could potentially physisorb (Coulombic and van der Waals coupling)[121]–[123] at the (negatively charged) MoS₂ cathode, resulting in a close encounter of the CO₂ molecules with the MoS₂ surface. The presence of EMIM⁺ cations around CO₂ molecules can reduce the reaction barrier for electrons passing into CO₂. Thus, the observed high CO₂ reduction reaction is attributed to a synergistic action of the MoS₂ catalyst and the EMIM-BF₄ ionic liquid. While EMIM-BF₄ plays a crucial role by reducing the overpotential for the reaction, the CO₂ reduction rate is mainly governed by the intrinsic properties of the MoS₂ catalyst. In addition, we measured the work function of MoS₂ through the use of ultraviolet photoelectron spectroscopy. The obtained results indicate that the work function of MoS₂ (3.9 eV) is significantly lower than that of the bulk Ag (4.37 eV) and Ag NPs (4.38 eV)[123]. Due to the low work function of MoS₂, the abundant metallic-like d-electrons in its edge states can take part in the reactions, ultimately resulting in the superior CO₂ reduction performance compared to Ag.

3.1.5. Vertically aligned MoS₂ nanosheet:

Now that we understand that the MoS_2 edges are responsible for the high CO_2 reduction reaction rate, we have synthesized a vertically aligned MoS_2 nanosheet[124], and observed another factor of two improvements on the CO_2 reduction performance.

3.1.5.1. Synthesize of Vertically Aligned MoS₂

Vertically aligned MoS₂ nanoflakes were grown by chemical vapor deposition (CVD) using a slightly modified method as reported previously[124]. At first, substrates (Glassy carbon) were thoroughly cleaned via rinsing in acetone, methanol and isopropanol solvents sequentially followed by drying in nitrogen flow. Next, a thin layer of molybdenum (5 nm) was deposited on the substrates by electron beam evaporation (Varian Evaporation System). For sulfurization, Mo deposited substrates were loaded in the center of a three zone furnace (MTI Corp. model OTF-1200X) consisting precise temperature and gas flow controller units. The sulfur precursor purchased from Sigma-Aldrich was placed in the upstream of the growing chamber where the maximum temperature reached to 200 °C, above than the sulfur melting point. Prior to heating process, the chamber was evacuated to 5 mTorr and then the argon (Ar) gas was purged through the chamber to force undesired gases out. Then, the center of the furnace was heated to 600 °C in 30 minutes and kept constant for next 15 minutes. During this growth process, Ar gas was continuously flown (200 SCCM) as a carrier gas. Finally, growth chamber was cooled down to ambient temperature under the protection of Ar gas flow and samples were taken out for further experiments. Physical and electrochemical characteristics of vertically aligned MoS₂ were characterized as previously discussed.

Figure 27a presents a HAADF and annular bright field (ABF) image of the vertically aligned MoS_2 nanosheets. While the MoS_2 layers are generally aligned perpendicular to the substrate surface, only a few select sheets can be found which are aligned parallel to

the electron beam to allow for atomic resolution imaging (Figure 27b). This image identifies the clearly-separated Mo and S atomic columns, as the Mo atoms are heavier and thus appear brighter. The proposed atomic structure of the Mo and S layers is superimposed on the atomic-resolution image in Figure 27b. While the nature of the terminating atoms in these MoS₂ nanosheets cannot be directly visualized in this orientation, previous results have shown that synthesized MoS₂ nanosheets are generally terminated by Mo atoms due to their low-energy state[45]. The vertically aligned MoS₂ samples were further characterized by Raman spectroscopy (Figure 27c). Two essential peaks are clearly visible at 385 (in-plane Mo–S phonon mode - E^{1}_{2g} mode) and 408 cm⁻¹(out-of plane Mo–S phonon mode - A^{1}_{g} mode) [45], [111], [124], [125] of out-of plain A^{1}_{g} phonon mode to E^{1}_{2g} mode is significantly high (~3), which clearly supports the existence of vertically orientated nature of MoS₂ flakes[124].

Figure 27d shows the CO₂ reduction performance of the vertically aligned MoS₂ obtained in similar experimental conditions (i.e., 96 mol% water and 4 mol% EMIM-BF₄). As expected, CO₂ reduction reaction initiated at low overpotential (54 mV) similar to bulk MoS₂. Additionally, further improvement has been observed within complete applied potential range (Figure 27d). In the low applied potential region, vertically aligned MoS₂ as shown in inset of Figure 27d. This trend remains also valid in the high potential region. At -0.764 V a remarkably high CO₂ reduction current density (130 mA/cm²) was recorded for vertically aligned MoS₂. The high catalytic performance of vertically aligned MoS₂ is attributed to the high density of active sites preferably Mo atoms available for the CO_2 reduction reaction. However, further efforts are needed to understand the nature of edge atoms in the vertically aligned MoS_2 responsible for CO_2 reduction performance.



Figure 28: Vertically aligned MoS₂ nanoflakes. (a) ABF STEM images of vertically aligned MoS₂ (scale bar, 20nm). STEM analysis (inset) shows the vertically aligned texture of MoS₂ nanoflakes (scale bar, 5nm). (b) RGB added image of (G+B) high-angle annular dark-field (HAADF) (R) inverted ABF STEM images of vertically aligned MoS₂. High resolution HAADF STEM image of vertically aligned MoS₂ (scale bar, 2nm). Mo atoms are brighter and larger in size in comparison to sulfur atoms due to high atomic number. (c) Raman spectrum for vertically aligned MoS₂. (d) CO₂ reduction performance of bulk MoS₂ and vertically aligned MoS₂ represented by VA MoS₂.

3.1.6. Summary and conclusion:

In summary, we have discovered that bulk MoS_2 - a non-precious catalyst and the most versatile member of TMDCs - exhibits the highest observed catalytic performance for the

 CO_2 reduction. The significantly higher CO_2 reduction current density (relative to noble metal catalysts) is mainly attributed to a high density of d-electrons in Mo-terminated edges and also to its low work function. We propose that TMDCs can successfully replace expensive noble metal electrodes, with the promise of higher CO_2 conversion rates and selectivity and can be the most attractive catalyst for future CO_2 reduction applications.

3.2. Transition metal dichalcogenides (TMDCs) for CO₂ reduction

3.2.1. Introduction

Electro- and photochemical reduction of carbon dioxide (CO₂) offer promising ways to conveniently recycle CO₂ into fuels[14], [126]–[131]. However, application of these processes has been advancing very slowly in the last two decades, mainly due to insufficient performance of existing catalysts[23], [86], [99], [132], [133]. Fundamentally, conventional and recently developed metal catalysts, e.g., metal nanoparticles[23], [86], [99] either require high overpotentials that result primarily from the weak binding interactions of the reaction intermediates to the catalyst, or have low exchange current densities due to the slow electron transfer reactions for CO₂ reduction. Both of these properties depend on not only the intrinsic electronic properties of the catalyst material, but also on the solvent and the architecture of the material. Recently, we have discovered that three-dimensional bulk MoS₂ in an ionic liquid (IL) is a promising CO₂ reduction catalyst with an extremely low overpotential (54 mV)[2], suggesting that the transition metal dichalcogenide (TMDC) class of materials holds great promise for CO₂ electrochemical reduction, if the activity can be increased without compromising the low
overpotential. Thus, we engineered nanoarchitectures, compositions and electronic structures of the TMDCs to achieve high performance for electrocatalytic CO_2 reduction.

In this paper we report on a novel 2D form of transition metal dichalcogenide (TMDC) that has extraordinary activity for catalyzing CO₂ reduction in the ionic liquid 1ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄). The new TMDC architectures, grown by chemical vapor transport (CVT) technique, are several layer thick nanoflakes with metal-terminated edges. Our results indicate that tungsten diselenide (WSe₂) nanoflakes are the most active catalyst for CO₂ reduction ever reported. Atomic level studies of WSe₂ NFs before and after electrochemical experiments using scanning transmission electron microscopy (STEM) indicate that edges of the WSe₂ NFs are tungsten (W) terminated and remain stable during the reaction. Density functional theory (DFT) calculations provide insight into the unique electronic properties of the TMDC NFs with metal edges that lead to the outstanding performance for CO_2 reduction. Our calculations reveal that the low overpotentials of these NFs result from the strong binding energies of key intermediates on the metal edges, and the high exchange current densities are correlated with the work functions of the TMDCs. The novel architectures of the TMDC NFs break through the limitations of previous catalysts for electrochemical CO₂ reduction.

3.2.2. Material synthesis and characterization

The TMDCs in this study are synthesized through direct reaction of the pure elements followed by a vapor transport process in an evacuated ampule at elevated temperatures (Figure 29). In this method, the powders of the transition metals and chalcogens (>99.99% trace metal basis purity) were mixed in desired stoichiometric ratio and loaded in a quartz ampule. The total loaded weight was about one gram and quartz ampule had one cm internal diameter and 20 cm length. The ampule was then evacuated with a turbo molecular pump ($<10^{-6}$ mbar) and sealed with a hydrogen torch. The ampule was then placed in a day. The temperature of the empty part of the ampule (cold zone) was then gradually cooled down to 950°C in four days, while the other end was maintained at 1080°C, in order to form single crystalline grains with pristine structure via direct vapor transport. The system was then slowly cooled down to room temperature in one day and the material was taken out for tests and characterizations. The crystalline grains were finally grounded before liquid exfoliation method.



Figure 29: An optical image of a crytaline structure of WSe₂ grown by chemical vapor transport (CVT) technique. (scale bar, $10 \mu m$).

TMDC nanoflakes were synthesized using an exfoliation method[134], [135]. The chemical vapor transport (CVT) grown TMDC crystalline grains e.g., MoS₂, MoSe₂, WS₂ and WSe₂ were grounded before liquid exfoliation. The nanoflakes were synthesized by sonicating a solution containing a mixture of 300 mg of powder (TMDCs) dispersed in 60 ml isopropanol solution. The sonication was carried out for 30 hours using a sonication probe (Vibra Cell Sonics 130 W). The obtained dispersions were centrifuged for 60 minutes at 2000 rpm. After centrigugation, the supernatant (top two thirds of the centrifuged solution) was collected by a pipette and stored in a glass vial. Figure 30 shows synthesized TMDC nanoflakes dispersed in the solvent.



Figure 30: Synthesized TMDC nanoflakes after 30 hours of sonication and an hour of centrifugation at 2000 rpm.

Dynamic light Scattering (DLS) experiments were carried out to measure flake sizes using the NiComp ZLS 380 system at 25°C. The instrument includes a 35 mW semiconductor laser with 670 nm emissions and a thermoelectric temperature control for samples. Synthesised TMDC NFs dispersed in isopropanol were used for DLS experiments. Typical error in DLS data is in the order of 5-8%. Figure 31 shows normal distributions of synthesized flakes for different TMDC NFs.



Figure 31: size distribution of synthesise TMDC flakes. The average size of ~ 100 nm were obtained for all TMDC NFs. Raman characterization of the TMDC NFs were shown in Figure 32. The data are obtained

with a HORIBA LabRAM HR Evolution confocal Raman microscope. The instrument was configured with a 532 nm laser source, 1200 g/mm grating, a Horiba Andor detector, and a 100x objective. Laser powers at the sample were between 1-15 mW. Integration times and averaging parameters were chosen to maximize signal-to-noise.



Figure 32: Raman characterization of the TMDC NFs. The peak positions are consistent with the observed spectra in the literature[136], [137], revealing that the flakes remain highly crystaline after the sample preparation.

SEM characterization of WSe₂ nanoflakes was carried out to understand the morphology at microscale (Figure 33). The instrument used for characterizing WSe₂ nanoflakes was integrated in a Raith e-LiNE plus ultra- high resolution electron beam lithography system. A distance of 10 mm was kept from the electron source and a voltage of 10 kV was used while imaging[138].



Figure 33: Scanning Electron Microscopy (SEM) of WSe₂ (scale bar, 2 μ m in the main image and 200 nm in the inset).

3.2.3. Electrochemical reduction of CO₂

CO₂ reduction performance of similar size (~ 100 nm) TMDC NFs including MoS₂, WS₂, MoSe₂ and WSe₂ was tested using a rotating disc electrode (RDE). All TMDCs were grown using chemical vapor transport technique. All experiments were performed inside a two-compartment three-electrode electrochemical cell using a 50 vol% of EMIM-BF₄ and water electrolyte. Two-compartment three-electrode electrochemical cell was used to perform CO₂ reduction reaction (Figure 34). The working electrode (WE), reference electrode (RE) and counter electrode (CE) were immersed into the 50 vol% ionic liquid solution (EMIM–BF₄ and water). The synthesized TMDC NFs (e.g., MoS₂, MoSe₂, WS₂, and WSe₂) coated on glassy carbon (GC) substrate, Platinum (Pt) gauze 52 mesh (Alfa Aesar) and Ag/AgCl (BASi) were used as working, counter and reference electrode, respectively. The cathode and anode part of the cell were separated through ion exchange membrane to eliminate the effect of product oxidation at the anode surface. All experiments were performed using rotating disk electrode (RDE) by submersing working electrode in the three electrode cell. To eliminate the effect of mass transport during the reaction working electrode was rotated at 1000 rpm rotating speed. The cell was connected to the potentiostat (CH Instruments) for electrolysis characterization. The potentiostat was connected to the computer through CH instruments software. A 6mm polyethylene tube was used to bubbling the gas (CO₂, 99.9% UHP from Praxair) into the electrolyte for 30 minutes prior to starting the experiment.



Figure 34: Schematic diagram of two-compartment three-electrode electrochemical cell.

Figure 35a shows cyclic voltammetry (CV) results of WSe₂ as well as Ag nanoparticles (Ag NPs) and bulk Ag as a representative of noble-metal catalysts. The polarization curves (i-V) were obtained by sweeping potential between +0.8 and -0.764 V vs RHE (Reference Hydrogen Electrode, all potentials reported here are based on RHE) with the scan rate of 50 mV.s⁻¹. The CO₂ reductions starts at -0.164 V (overpotential of 54

mV) confirmed by Faradaic efficiency (F.E.) measurements (inset Fig. 35). At -0.764 V potential, the recorded current density for synthesized WSe₂ NFs (330 mA. cm⁻²) is 100 and 30 fold higher than that of bulk Ag (3.3 mA.cm⁻²) and Ag NPs (11 mA.cm⁻²), respectively. The measured F.E. shows that WSe₂ NFs/IL is highly selective for CO formation at high overpotentials (-0.264 to -0.764 V). However, at smaller overpotentials (-0.164 to -0.264 V) it produces a mixture of CO and H₂ (synthetic gas). Figure 35b show respectively the results of CV for all TMDCs tested in this study.



Figure 35: CO₂ reduction performance of the TMDCs catalysts, Ag NPs and bulk Ag in the EMIM-BF4 solution: (a) Cyclic Voltammetric (CV) curves for WSe₂ NFs, Ag nanoparticles (Ag NPs) and bulk Ag in CO₂ environment. The experiments were performed in 50 vol% EMIM-BF₄ solution by sweeping applied potential from +0.8 V to -0.764 V vs RHE. CO and H₂ Faradaic Efficiency (F.E.) at different applied potentials for WSe₂ NFs (inset). The F.E curve indicates the low overpotential (~54 mV) for CO₂ reduction.(b) Catalytic performance of TMDCs in 50 vol% EMIM – BF₄ and water electrolyte. Carbon Dioxide was bubbled into the ionic liquid solution for 30 minutes prior to the experiment. The polarization curves (i-V) for the synthesized TMDC catalysts were obtained by sweeping the potential between +0.8 and -0.764 V vs RHE (Reference hydrogen electrode) at 50 mVs⁻¹.

The CO₂ reduction performance of different TMDC nanoflakes - WS₂, MoS₂, MoS₂, and

WSe₂ were examined in 50 vol% EMIM-BF₄ and water electrolyte solution at different

potentials. Figure 36a-d show the variation in the faradaic efficiency of CO and H_2 formation for MoS₂, MoSe₂, WS₂, and WSe₂. The product analysis for the electrochemical experiments was carried out using an SRI 8610C GC system equipped with 72 ×18 inch S.S molecular sieve-packed column. A thermal conductivity detector was used to analyze and differentiate the injected samples. Ultra-high purity helium gas (purchased from Praxair) was used to detect CO and ultra-high purity nitrogen (purchased from Praxair) was used to detect H₂.



Figure 36: Faradaic Efficiency (F.E.) measurement for different TMDC nanoflakes (NFs) A-D TMDC nanoflakes - WS₂, MoS₂, MoS₂ and WS₂

TMDC NFs catalytic performance was compared with that of existing catalysts in the literature (Figure 37) by multiplying current density (activity) by CO formation F.E. (selectivity). Interestingly, WSe₂ NFs exhibit extraordinarily performance especially at lower overpotentials. For instance, at 100 mV overpotential, WSe₂ NFs shows almost two orders of magnitude higher performance compared to bulk MoS₂ and Ag NPs tested under identical conditions inside an ionic liquid environment. The WSe₂ NFs performance is also three orders of magnitude higher than those of Au NPs[94] and Cu NPs[13], respectively. Additionally, at this overpotential WSe₂ shows about three and two fold higher performance compared to WS₂ and MoSe₂ NFs, respectively (Figure 37). WSe₂ NFs also exhibit remarkable performance over the entire range of overpotential compared to all noble metal catalysts which makes it the best candidate among existing catalysts for CO₂ reduction (Figure 37).



Figure 37: Overview of different catalysts' performance at different overpotentials (η). All TMDCs (i.e., MoS₂, WS₂, MoSe₂ and WSe₂) and Ag nanoparticles (Ag NPs) were obtained in the identical conditions. Other catalysts' data were taken from the reference[2].

Next, we performed electrochemical impedance spectroscopy (EIS) at 150 mV above the CO₂ reduction onset potential to measure the charge transfer resistance (R_{ct}) for WSe₂ and other studied catalysts [7], [10], [89]. A charge transfer resistance is correlated to the amount of electron transferred from the catalyst surface to the reactant[139]–[141] as well as to the intermediate formation inside the double layer[10], [89]. Results shown in Figure 38 demonstrate a much smaller value of R_{ct} (~ 180 Ω) for WSe₂ NFs compared to Ag NPs (~ 550 Ω) under identical experimental conditions. The R_{ct} value also significantly decreases with the increment in overpotential of the reaction (Figure 39).



Figure 38: EIS experiment with WSe₂ NFs and Ag NPs at 150 mV CO₂ reduction overpotential. The results show a much smaller (~ 180 Ω) R_{ct} for WSe₂ NFs compared to Ag NPs (~ 550 Ω).



Figure 39: Electrochemical Impedance Spectroscopy (EIS) measurement for WSe₂ NFs insideionic liquid at different over-potentials. (A) obtained data (B) fitted data.

Additionally, ultraviolet photoelectron spectroscopy (UPS) was employed to measure the work function of WSe₂ and other TMDCs[23] (Figure 40). Our results indicate a considerably lower work function of WSe₂ NFs (3.52 eV) compared to that of Ag NPs (4.38 eV) confirming the EIS data. These results provide strong evidence of the superior electronic property of WSe₂ resulting in a faster electron transfer and consequently a higher catalytic activity during the CO₂ reduction reaction.



Figure 40: Experimental Work function measurement for Ag nanoparticles (Ag NPs) and TMDCs.

To characterize the atomic arrangement of edge atoms, STEM analysis was performed on several liquid exfoliated, mono- and multi-layers of WSe₂ NFs (Figure 41a). The line intensity profile of single layer WSe₂ NF (Figure 41b) indicates that the edges of the nanoflakes are W terminated. Moreover, STEM analysis on the edge atoms after 27 hours of chronoamperometry (CA) experiment indicates a stable atomic structure of W edge sites (Figure 41c-d). These results suggest that transition metals with d-orbital electrons on the edge sites mainly contribute to the CO₂ reduction without any evidence of instability over time.



Figure 41: Scanning Transmission Electron Microscopy images of WSe₂. (a) STEM image of WSe₂ (scale bar, 2 nm) and (b) Intensity profile of the flake before electrochemical experiment (c) STEM images of WSe₂ nanoflake (scale bar, 2 nm) and (d) Intensity profile of the flake after 27 hours chrono-amperometry experiment.

Long term stability of WSe₂ NFs were studied by performing chronoamperometry experiment (CA) in a three-electrode two-compartment cell using the same method and materials as explained in section S5. A 6mm polyethylene tube was used to continuously bubble the gas (CO₂, 99.9% UHP from Praxair) throughout the entire length of the experiment into the electrolyte. A magnetic stirrer was placed into the electrolyte solution to evade any mass transport issues. Stability of the catalyst was recorded for prolonged period (27 hours) by running the cell at potential of -0.364 V (0.2 V overpotential) using Voltalab PGZ100 potentiostat (purchased via Radiometer Analytical SAS) calibrated with a RCB200 resistor capacitor box. The potentiostat was connected to a PC using Volta Master (Version 4) software[138].

Figure 42 shows the stability of the WSe₂ NFs. The spikes observed along the current density vs time curve are mainly due to the fluctuations in the flow rate of the CO₂ being bubbled into the electrolyte solution.



Figure 42: stability test of WSe₂ NFs in 50 vol% IL at potential 0.364 V (0.2 V overpotential). The chronoamperometry experiment indicate only 10% decay after 27 hrs.

X-ray photoelectron spectroscopy (XPS) data further verify the long term stability of the catalyst (Figure 43)[2]. XPS experiments were carried out using Thermo Scientific ESCALAB 250Xi instrument. The insstrument was equipped with an ellectron flood and scanning ion gun. All spectra were calibrated to the C1s binding energy at 284.8 eV.



Figure 43: X-ray photoelectron spectroscopy (XPS) spectra of WSe₂ NFs (A) before electrochemical experiment (B) after 27 hrs of chronoamperometry experiments. The Spectra show standard W $4f_{7/2}$ (~32.6 eV) and $4f_{5/2}$ (~34.7 eV) peaks consistent with the presence of W⁺⁴ in WSe₂ structures. A small variation in the tungsten oxides (~36.8 eV) surface area (~ 14%) indicates high stability of WSe₂ after 27 hrs CA experiment.

3.2.4. Photo-Electrochemical reduction of CO₂

The performance of WSe_2/IL was also studied in the photochemical process using a custom made wireless setup. The details of the setup and materials are discussed in the section 3.2.4.1 to 3.2.4.5.

3.2.4.1. methods and materials

All chemicals were used as received without any purification unless required. Cobalt nitrate hexahydrate ((Co(NO₃)₂.6H₂O), Alfa Aesar), Potassium based buffer solution (0.071 M KPi, pH=7, Sigma-Aldrich), Nafion 117 (10.0 cm \times 10.0 cm, FuelCellsEtc) were purchased from the indicated supplier. Triple a-Si solar cells were purchased from Xun-light Corp. (Toledo, OH). The acrylic plastic used for building the phot-reduction chamber was purchased from Total Plastics Inc (CHEMCAST GP).

3.2.4.2. Custom Made Wireless solar Cell setup

The photochemical chamber as shown in Figure 44 and 45 is an acrylic plastic based transparent chamber that was machined according to the required dimensions and assembled together using acrylic glue. The transparent chamber is separated into two compartments by two tandem amorphous silica based triple junction (a-Si/a-SiGe/a-SiGe) photovoltaic (PV) cells connected through a copper tape and a piece of nafion membrane (Figure 45). Silicon was chosen for the artificial leaf experiment due to its earth abundance and application across various fields. The illuminated side of PV cells was electrodeposited with another Earth abundant metal cobalt (Co) catalyst to initiate oxygen evolution reaction (OER)[142]. Cobalt is well known Earth abundant metal and its self-healing properties make it a suitable candidate for oxygen evolution reaction (OER) [143], [144]. Cobalt coated ITO (light illuminated side) side of the solar cell forms a photo-anode and is dipped with Potassium based buffer solution (0.071 M KPi, pH=7), is responsible to initiate water splitting reaction[145]. The back stainless substrate of the solar cell was coated with synthesized WSe₂ nanoflakes (NFs) using drop casting coating method. This WSe₂ coated stainless steel substrate forms the photocathode and is placed in a 50 vol% EMIM-BF₄ in water electrolyte solution[131] which is saturated with CO₂ prior to the experiment. WSe₂/IL co-catalytic system worked towards the conversion of CO₂ to CO. The nafion membrane treatment was done using standard activation treatment in using 5 wt% KOH solution so as to keep the membrane active in the solution. This membrane acts as a barrier in the photo chamber separating the two electrolytes and permeating only H⁺ ions generated through OER to transfer to the other compartment to participate in the CO₂ reduction reaction[25].



Figure 44: A schematic of custom made solar cell setup.



Figure 45: Schematic of the Photochemical Chamber. (1) two PV cells in series connected by a copper tape, (2) Cobalt coated on ITO, (3)Potassium Phosphate buffer solution,(4)Nafion (117) Membrane, (5) 50 vol% EMIM-BF₄ solution, , (6)WSe₂ on Stainless Steel substrate(drop casting), (7)Gas bubbles generated through chemical reaction.

3.2.4.3. Co-OEC Electrodeposition

Co–OEC was electrodeposited onto the ITO surface of the solar cell from cobalt (II) nitrate hexahydrate (Co(NO₃)₂.6H₂O, Alfa Aesar). The electrodeposition was carried out using a solution prepared by mixing 73 mg of cobalt nitrate hexahydrate (Co(NO₃)₂.6H₂O, Alfa Aesar) in 500 ml of 0.071 M potassium phosphate (pH 7) using a three–electrode cell configuration comprising of ITO working, platinum mesh as counter and Ag/AgCl reference electrode. The solar cell was placed in the Co – Pi solution and the deposition process took place for 5 minutes. The electrodeposition was done by running the three electrode and solar cell configuration in a chronoamperometry experimental setting at 1.5 V vs Ag/AgCl without stirring and without any i-R compensation. New solutions were prepared for each experiment. The stainless steel substrate of the solar cell was not supposed to be coated with Co and hence was wrapped up in scotch tape.

3.2.4.4. WSe₂ Drop Casting

After the solar cell was electrodeposited with cobalt, the back stainless steel substrate of the solar cell was coated with synthesized WSe₂ nanoflakes through drop casting. The synthesis process is described in the material synthesis section of the SI file. The stainless steel surfaced was initially roughed up by using sand paper to enable appropriate adhesion of the catalyst to the surface. The catalyst ink was continuously drop casted on the stainless steel substrate and was allowed to dry until the isopropanol evaporates from the surface and a fine uniform coating of MoS₂ developed.

3.2.4.5. Preparation of Ionic Liquid

Prior to starting any of the photo-reduction experiments, pure ionic liquid was diluted with water in appropriate amounts to achieve 50 vol% EMIM–BF₄ in water. CO₂ (99.9% UHP, Praxair) was flown at 1 ml/min using a mass flow controller and was directed into the EMIM–BF₄/water electrolyte for 30 minutes so as to saturate the ionic liquid with CO₂.

3.2.4.6. Results and discussion

Figure 44 and 45 show the schematic diagram of our system. As discussed in section 3.2.4.1 to 3.2.4.5, the cell is composed of three major segments (i) multi-junctions solar cells to collect sun energy, (ii) the WSe₂/IL co-catalyst system on the cathode side for CO₂ reduction and (iii) Cobalt (Co²⁺) catalyst on the anode side to perform the oxygen evolution reaction (OER)[142], [144], [146]. In this platform, an amorphous silicon based triple junction photovoltaic cell (PV-a-si-3jn) was employed to generate the required potential for the reaction upon exposure to a light source, ranging from visible light to near infrared. It is worth noting that two PV-a-si-3jn cells were connected in series to overcome the CO₂ reduction thermodynamic barrier (Figure 44, section 3.2.4.2). Figure 46 shows the calculated mole of products with respect to the number of the sun illumination of air mass (AM) simulated sun light. The accumulated number of CO and H₂ follows approximately a 10:1 ratio for the entire range of sun illumination.



Figure 46: (A) Number of mole of product with respect to different sun illuminations after 60mins experiments. (B) Calculated solar to fuel efficiency (SFE) of photochemical process using WSe₂/IL co-catalyst system. Our calculation indicates ~ 4.6% SFE, which is limited by the maximum efficiency of PV-a-si-3jn (~ 6.0%).

This is consistent with our F.E. result obtained at higher overpotentials in the three electrode electrochemical setup. We also measured the solar-to-fuel conversion efficiency (SFE) for our photochemical process using equation 3. The solar to fuel (SFE) of our system was determined in terms of gas product using the analyzed data from the GC. In addition to being dependent on the intensity of the incident solar irradiance, the gas generation rate is also proportional to the catalytic surface area (i.e., WSe₂ doped surface area) and most importantly the SFE of the solar cell. The GC results indicate that H₂ and CO are the only products produced by the chemical reaction. Hence, SFE could be calculated by using the equation 3,

$$\eta = \frac{N_1. E_1 + N_2. E_2}{\underbrace{U_g. A_{cat}}}$$

where, N_1 and N_2 are number of moles of produced gas per unit of time (mol/s) measured using GC, E_1 and E_2 are Energy Densities of the corresponding gas (kJ/mol), A_{cat} is Catalytic surface available for the reaction (m²), U_g is total solar irradiance (mW/cm²).

Figure 46b shows the SFE with respect to the number of the sun illumination. Our calculation indicates ~ 4.6% SFE which is limited by maximum efficiency of PV-a-si-3jn [144] (~ 6.0%, section 3.2.4.7). The obtained SFE is noticeably higher than that of the water splitting reaction (~2.5%) previously measured using an identical triple junction photovoltaic cell[144].

3.2.4.7. PV efficiency measurement

The solar to electricity conversion efficiency of triple-a-Si PV cell coated with Co catalyst was measured under one sun simulated sunlight illumination. The voltage produced by a PV cell was directly measured with a multimeter while the resistance of the circuit was changed using variable resistors. An open circuit voltage (V_{oc}), a short circuit current and the average fill factor of PV cell were 2.12 V, 6.1 mA/cm² and 0.55 respectively. Therefore, the dry cell efficiency of 7.1% can be calculated by dividing the product of the above three parameters by the one sun illumination (100 mW/cm²). V_{oc} of two PV cell in series configuration was 3.6 V, which was observed to drop to 3Vwhile the short circuit current remained unchanged when the cell was brought to inside of electrolyte solution. The fill factor was assumed to change rarely within the experimental range. Based on the measurement, the change in V_{oc} affected the PV efficiency that could be reasonably predicted as high as 6% in the electrolyte.

3.2.5. Mechanistic study and DFT calculation

DFT calculations were performed to gain insight into the outstanding activities of the TMDC NFs. The calculated reaction free energies of $CO_2 \rightarrow CO$ pathway using computational hydrogen electron approach at zero potential[147] show that the formation of COOH* is endergonic and is the rate-limiting step for both Ag (111) and the Ag55 cluster (Figure 47). The Ag55 cluster requires less energy to form COOH* than Ag (111), due to the presence of under-coordinated Ag atoms of the cluster.



Figure 47: (a) Calculated free energy diagrams for CO_2 electro-reduction to CO on Ag(111), Ag₅₅ NPs, MoS₂, WS₂, MoSe₂ and WSe₂ NFs at 0V electrical potential. (b) Calculated partial density of states (PDOS) of the d band (spin up) of the surface Ag atom of Ag₅₅ and (c) surface bare metal edge atom (W) of the WSe₂ NFs.

This explains the enhanced activity of Ag nanoparticles compared to bulk Ag, in agreement with other studies[86]. The fact of COOH* formation being endergonic is also true for other metal surfaces such as Pd, Au and Cu[148]–[150]. However, on the metallic edges of the TMDC NFs, COOH* formation is highly exergonic due to the strong binding

to the TMDC metal edge sites. The CO* also becomes much more stable on the TMDC NFs than that on the Ag systems, and shows a small energy change from COOH*. This suggests that the CO₂ electrochemical reduction is kinetically more favorable on the TMDC NFs than that on the Ag systems since it is not limited by the difference of energies of the intermediates (Figure 47) resulting in low overpotential. In addition, the calculated projected density of states (PDOS) of the edge metal atom (Mo or W) reveals that the d band centers of these metal edges are much closer to the Fermi level than those of the Ag (111) surface further supporting the high catalytic activities of the TMDC NFs (Figure 47b-c and Figure 48a-d) according to the d band theory. The d band theory[120], [151] states that the higher the d band center, the more active the metal.



Figure 48: Calculated partial density of states (PDOS) of the d band (spin up) (A-C) surface bare metal edge atom (Mo and W) of the MoSe₂, MoS₂ and WSe₂ NFs, respectively, and (**D**) the surface Ag atom of bulk Ag(111)

Nevertheless, comparison of the energetic pathways of the four TMDCs did not explain the trend of their catalytic activities. Thus we calculated the work functions of the monolayers of the four TMDCs, as shown in Figure 49. Our calculations show a clear trend of $MoS_2 > WS_2 > MoSe_2 > WSe_2$, consistent with UPS results (Figure. 40, section 3.2.3). This indicates that the electron transfer from the metal edge to the adsorbates should become easier/faster when going from MoS_2 to WSe_2 [152]. Because the initial step of CO_2 reduction, the activation of CO_2 , involves electron transfer from the electrode to CO_2 , electrodes with smaller work functions essentially lead to easier/faster CO_2 activation. In this case, WSe_2 is the best TMDC for CO_2 activation among the tested materials. This well explains the observed trend for the experimental current densities.



Figure 49: Theoretical Work function calculations for TMDC monolayers.

In addition to the unique catalytic properties of the TMDC NFs, ionic liquids were found to play multiple roles in CO_2 electrochemical reduction. A previous study has suggested that ionic liquid molecules attached to the electrode surface could help to prevent the formation of oxalates by isolating the catalytic sites for CO_2 reduction[153]. Our previous study also suggested that the EMIM⁺ ion helps carry CO_2 to the catalyst surface by forming a complex with CO_2 in acidic conditions[2]. In this work we found that EMIM⁺ ions that attach to the metal edge of the TMDC NFs could weaken the binding of CO and possibly facilitate the CO desorption reaction (Figure 50). In particular, our calculations show that the bare metal edges of the TMDC NFs show strong chemisorption interactions with the EMIM⁺ ions in the presence of extra electrons on the surface (Table 3), while Ag surfaces did not bind EMIM⁺ ions.

Table 3. Reaction free energies of clean vs. IL covered TMDC NFs. IL ions covering the edges weaken the binding energies of the adsorbates.

System	$CO_2 + H^+ + e^- + * \rightarrow$	$COOH + H^+ + e^- \rightarrow$	$CO^* \rightarrow CO + ^*$
	COOH*	$CO^* + H_2O$	
MoS ₂ NFs	-1.556	0.180	1.380
MoSe ₂ NFs	-1.507	0.189	1.321
WS ₂ NFs	-2.031	0.337	1.698
WSe ₂ NFs	-1.857	0.310	1.550
MoS ₂ -IL NFs	-1.091	-0.048	1.143
MoSe ₂ –IL	-1.024	-0.052	1.079
NFs			
WS ₂ -IL NFs	-1.510	0.014	1.499
WSe ₂ -IL NFs	-1.463	0.077	1.389



Figure 50: Optimized geometries of Ag (111) and TMDC nanoribbons (covered by EMIM) and important intermediates in CO_2 electro-reduction to CO.

The coverage of the EMIM⁺ ions on the metal edges of the TMDC NFs results in the isolation of W atoms exposed on the edge. This leads to weaker binding interactions of the intermediate adsorbates compared to the uncovered clean metal edges (Fig. 51). Thus, in addition to preventing side reactions and carrying CO_2 molecules, ionic liquid ions that attach to the metal edge of the TMDC NFs could enhance the turnover frequency of the reaction.



Figure 51: Reaction pathways of clean vs. IL covered WSe₂ NFs.

3.2.6. Summary and conclusion:

In summary, this study has demonstrated that TMDC NFs in the ionic liquid EMIM-BF₄ work as the most effective catalysts for CO₂ reduction. Cyclic voltammetry results show superior reaction rates for the WSe₂ NF catalyst among all other TMDC NFs (MoS₂, WS₂ and MoSe₂) under identical experimental conditions. The WSe₂ NFs also perform extremely well compared with common noble metal catalysts (e.g., Ag and Au) with twothree orders of magnitude higher activity at low overpotentials. Atomic scale characterizations (STEM) and DFT calculations were used to elucidate electronic and catalytic properties of TMDCs, suggesting that the exposed metal edge sites (Mo and W) are contributing to high activity. The TMDC NF catalysts discovered in this work, especially WSe₂, provide promising new opportunities for converting CO₂ into solar fuels.

4. CHAPTER 4: Li-Oxygen battery

Li-oxygen batteries are considered a possible alternative to Li-ion batteries for the future energy storage systems due to their high specific energy[31], [154]. Fundamentally, the specific energy and rechargeability of Li-O₂ batteries are governed by the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) rates at the cathode and their corresponding overpotentials[155]. Numerous materials, such as carbon nanostructures [156], expensive noble metals [33], [34], and metal oxides [55], [157] have been used as catalysts for battery applications. Among these, doped carbon nanomaterials[158], [159] (e.g., graphene, carbon nanotube, and Super P) have shown remarkable performance for the oxygen reduction reaction (ORR). However, the degradation of the carbon as well as the electrolyte during cycling, e.g., formation of the side products such as carbonates limits the benefit of their ORR characteristics[30], [35], [60], [160]. Carbon free catalysts, such as noble metals [35], [60] and metal oxides (e.g., Co_3O_4), [161] have shown excellent stability, but exhibit only either superior ORR or OER performance. Thus, finding a highly active and reversible bi-functional carbon free catalyst that works in concert with the electrolyte remains one of the key challenges for the development of Li-O₂ batteries.

Recently, two dimensional molybdenum disulfide (MoS_2) has been employed in different electrochemical systems such as the hydrogen evolution reaction (HER)[111]⁻[5], carbon dioxide conversion[2], and ORR[162] due to its prominent catalytic features (e.g., activity and stability). In the context of this dynamic research field, we report results for MoS_2 nanoflakes (NFs) that exhibit unique bi-functional catalytic activity for both ORR and OER in the ionic liquid (IL) 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄). Our cyclic voltammetry (CV) results indicate that the MoS₂ performance exceeds that of noble metals in either case when tested under identical experimental conditions. This MoS₂/IL system is also found to perform remarkably well in a Li-O₂ battery system with a high round trip efficiency, small discharge/charge polarization gap and good reversibility.

4.1. Material synthesis and characterization

The MoS₂ NFs were synthesized using a modified liquid exfoliation method (see section 3.2.2[163], [164]The scanning electron microscopy (SEM) image of synthesized MoS₂ NFs deposited on gas diffusion layer (GDL) substrate is shown in Figure 52a. The higher magnification of the SEM image (inset of Figure 52a) further shows the surface morphology of the deposited catalyst confirming highly packed randomly oriented MoS₂ NFs. In addition, dynamic light scattering (DLS) experiments were also performed to determine the size of synthesized nanoflakes (see section 3.2.2). The DLS analysis indicates a uniform size distribution of synthesized MoS₂ NFs in a narrow range (110-150 nm) with an average flake size of 135 nm (Figure 52b). The inset of Figure 52b shows the Raman spectrum of the synthesized flakes with two distinct MoS₂ peaks between 300 and 500 cm⁻¹. The first peak at ~382 cm⁻¹ occurs due to the E¹_{2g} phonon mode (in-plane) and the second peak at ~ 409 cm⁻¹ corresponds to the A_{1g} mode (out of plane)[125], [165].



Figure 52: Structural and elemental analysis of synthesized MoS₂ NFs, (a) SEM images of MoS₂ NFs deposited on the gas diffusion layer (GDL) (inset, scale bar, 100 nm) (b) Dynamic light scattering (DLS) and Raman spectroscopy of MoS₂ NFs (inset). (c) Low magnification low-angle annular dark field (LAADF) STEM image of a MoS₂ nanoflake approximately 200 x 150 nm in size supported on a lacey carbon film (scale bar, 50 nm), corresponding line profile along to the red dotted line (inset), and selected area electron diffraction (SAED) pattern (inset upper-right corner). (d) High resolution STEM image of MoS₂ NF edges (scale bar, 2 nm); the edges of the MoS₂ nanoflakes are terminated along the (100) and (010) crystallographic planes with the Mo atoms making up the edge of the MoS₂ monolayers. (e) Electron energy loss spectra (EELS) of the sulfur L-edge on the plane and edge of monolayer MoS₂. (f) The normalized pre-peak intensity as a function of layers in MoS₂ and at the edge of the monolayer MoS₂.

The MoS_2 NFs were further characterized at atomic scale by performing high resolution scanning transmission electron microscopy (STEM) experiments. Figure 52c shows a low magnification low-angle annular dark field (LAADF) image of a MoS_2 nanoflake approximately 200 x 150 nm in size, supported on a lacey carbon film. A typical hexagonal selected area electron diffraction (SAED) pattern (inset of Figure 52c) taken from the same MoS₂ nanoflake reveals its defect free and single phase crystalline layer structure. Moreover, an intensity profile corresponding to a line drawn from the vacuum to the center on the imaged flake shows the steps associated with the mono-, bi and tri-layer MoS₂ (inset of Figure 52c). We also imaged the edge state of a synthesized monolayer MoS₂ nanoflake. As seen in Figure 52d, the edges of the MoS₂ nanoflake terminate along the (100) and (010) crystallographic planes, with Mo atoms making up the edges.



Figure 53: Electron energy loss spectra (EELS) of the sulfur (S) *L*-edge as a function of MoS_2 layers for multi-layer MoS_2 and for the edge of the monolayer MoS_2 .

Next, we acquired electron energy loss spectra (EELS) of the sulfur (S) L-edge on the plane structure of mono- and multi-layer flakes as well as for the edge of monolayer MoS_2 (Figure 53). Usually, the pre-peak intensity at 162 eV energy loss (Figure 52e) is associated with transitions from the S $2p^{3/2}$ initial states to the conduction band[166], and inversely scales with the density of available charge carriers. Figure 52f shows the normalized peak

intensity as a function of layers in MoS_2 and at the edge of the monolayer MoS_2 . Results indicate a nearly 10-fold decrease at the Mo edge of the monolayer, while there is no noticeable difference as a function of MoS_2 layer away from the edge (Figure 52f). This measurement provides direct evidence for the remarkably high density of electrons at the Mo edges, which are believed to be the responsible sites for the electrochemical reactions[2].

4.2. Electrochemical characterization of the MoS₂/IL system

In order to study the catalytic activity of MoS₂ NFs for ORR and OER, electrochemical experiments were carried out in a standard three-electrode electrochemical cell. To prepare the cathode electrode, 0.3 mg of catalysts (synthesized MoS2 NFs, Pt NPs and Au NPs dispersed in IPA) were coated layer by layer onto a 1.5 cm2 Toray carbon paper (TGP-H-030, purchased from FuelCellsEtc) as a gas diffusion layer (GDL) and dried in the vacuum chamber at 120°C for 24 hrs. The Li wire (99.9% metal basis, Alfa Aesar) was used as counter electrode. 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF4), dimethyl sulfoxide (DMSO) and tetraethyleneglycol dimethylether (TEGDME) and Lithium Bis(Trifluoromethanesulfonyl) Imide (LiTFSI) salt were purchased through Sigma-Aldrich. The applied voltage was swept between 2 and 4.2 V vs. Li/Li+ with different scan rates. Cyclic voltammetry (CV) curve was then recorded using a Voltalab PGZ100 potentiostat (purchased via Radiometer Analytical SAS) calibrated with a RCB200 resistor capacitor box. The potentiostat was connected to a PC using Volta Master (version 4) software. The current densities, representing the oxygen electrode apparent activity, are

normalized with respect to the geometrical surface area. Figure 54a shows the CV curves recorded in Argon (Ar) and oxygen (O₂) saturated 0.1M LiTFSI IL electrolyte at 20 mV/s scan rate by sweeping the potential between 2.0 V to 4.2 V vs Li/Li⁺ (in the present study, all potentials are reported based on Li/Li⁺). These experiments were performed inside the argon (Ar) filled glove box (method section). In the Ar environment, MoS₂ NFs exhibit merely a featureless curve in both ORR and OER regions (Figure 54a). In contrast, MoS₂ NFs show a maximum ORR apparent activity (current density of 10.5 mA.cm⁻²) at 2.0 V together with a remarkable OER (5.04 mA.cm⁻²) at 4.2 V in O_2 saturated IL. However, the catalytic performance of the MoS₂ NFs is relatively poor in dimethyl sulfoxide (DMSO)[34], [167] and tetraethylene glycol dimethyl ether (TEGDME), [168], [169] which are commonly used electrolytes in the Li-O₂ battery systems (Figure 54b). In the case of MoS₂ NFs/DMSO, only -0.75 mA.cm⁻² (ORR) and 1.2 mA.cm⁻² (OER) current densities were recorded at potentials of 2.0 and 4.2 V, respectively. The current density also remained lower than 0.5 mA.cm⁻² for both ORR and OER at the same potentials for the MoS₂ NFs/TEGDME system. These results indicate a strong synergy of MoS₂ NFs and IL for both ORR and OER.

We also performed additional electrochemical experiments with Pt (100 nm) and Au (120 nm) nanoparticles in O_2 saturated IL under identical experimental conditions. Figure 54c indicates that the ORR apparent activity of MoS_2 NFs exceeds that of Pt NPs (~7 mA.cm⁻²) and Au NPs (4.5 mA.cm⁻²).



Figure 54: Cyclic voltammetry (CV) study of $MoS_2 NFs$, (a) CV curve obtained in O_2 and Ar saturated IL (Scan rate - 20mv/s). (b) ORR and OER performance of $MoS_2 NFs$ in O_2 saturated DMSO and TEGDME. (c) Comparison of ORR, and (d) OER for GDL, Au nanoparticles (Au NPs), Pt nanoparticles (Pt NPs) and $MoS_2 NFs$.

Except for mesoporous perovskite (La_{0.5}Sr_{0.5}CoO_{2.91}) nanowires catalysts[170] tested using a rotating disk electrode (RDE), our results also exceed those of other advanced catalysts such as metal oxides (e.g., Mn_3O_4)[171], noble metals (e.g., Au and Pd), and doped or functionalized carbon nanomaterials (e.g., n-doped graphene)[172] studied in the aprotic media (Figure 55a). Additionally, the OER results shown in Figure 54d clearly demonstrate the superiority of the MoS_2 NFs over Pt and Au nanoparticles at all potentials ranging from a thermodynamic potential of 3.0 V up to 4.2 V. It should be noted that at 4.2 V, the OER current density recorded for $MoS_2 NFs$ (5.04 mA.cm⁻²) is more than one order of magnitude higher than those for Au NPs (0.3 mA.cm⁻²) and Pt NPs (0.5 mA.cm⁻²). At the same potential, this performance of $MoS_2 NFs$ is also significantly higher than that of pervoskite nanoparticles (1.0 mA.cm⁻²) and highly active mesoporous perovskite nanowires (4.6 mA.cm⁻²)[170] (Figure 55b).



Figure 55: MoS₂ NFs performance compared with most common catalysts for (a) ORR and (b) OER. The results are exceeding the performance of advanced catalysts such as metal oxides (e.g., Mn_3O_4)[171], noble metals (e.g., Au and Pt)[35], and doped or functionalized carbon nanomaterials (e.g., n-doped graphene)^{Error! Reference source not found.} in protic media. The mesoporous perovskite (La_{0.5}Sr_{0.5}CoO_{2.91}) nanowires catalyst, studied by rotating disk electrode (RDE)[170] is an exception for ORR. Current densities were normalized with respect to the geometrical surface area.

To characterize Pt, Au and MoS₂ NFs catalytic activity we applied a roughness factor (RF) measurement to determine the catalyst's number of active edge sites. The RF number of the catalyst is determined by comparing their double layer capacitor (C_{dl}) with a flat standard capacitor[111], [173], [174] (Table 4). The CV experiments at different scan rates e.g., 20, 50, 100, 150 and 200 mV.s⁻¹ were performed in the 0.5M H₂SO₄ to calculate the C_{dl} of each catalyst[4] (Figure 56a-c). Figure56d-f shows the extracted C_{dl} values of 12.6,
7.5 and 2.13 mF.cm⁻¹ with respect to scan rate at the potential of +0.4 vs RHE for Pt, Au and MoS₂ NFs, respectively. These results were further confirmed by Electrochemical Impedance Spectroscopy measurement. Moreover, RF values of 630, 250 and 36 were obtained for Pt, Au and MoS₂ NFs catalysts, respectively. The calculated number of active sites for each catalyst was obtained using equation 1 (see section 2.3).

Catalyst	flat standard[7], [173], [174] capacitor (μF.cm ⁻²)	double layer capacitor (mF.cm ⁻²)	Roughnes s factor	# active sites
Pt	20	12.6	630	1.64×10 ¹⁸
Au	30	7.5	250	7.56×10 ¹⁷
MoS ₂ NFs	60	2.13	36	4.07×10 ¹⁶

Table 4. Number of active sites for Pt, Au and MoS₂ NFs catalyst



Figure 56: Active site measurement of Pt, Au, and MoS2 NFs in IL electrolyte a-c) cyclic voltammetry (CV) curves of Pt, Au, and MoS₂ NFs at different scan rates. The experiment was performed at 0.5 M H₂SO₄ electrolyte by sweeping potential between 0 to +0.3 V vs RHE (non-faradic region). (d-f) Current density of CV experiment at overpotential +0.2 V vs RHE as a function of scan rates. The slope of this line shows double layer capacitor for each catalyst system.

Additionally, the turn over frequency (TOF) of active sites for ORR in the Pt, Au and MoS₂ NFs inside the ionic liquid (EMIM-BF₄) were calculated at different over-potentials using equation 2[5], [7], [9]: Interestingly, the results clearly confirm that the MoS₂ NFs/IL catalyst system has ~ two order of magnitude higher TOF compared with Pt/IL and Au/IL catalysts in the all range of over-potentials (Figure 57a-b). However, the number of active sites in MoS₂ is much lower than those of Au and Pt.



Figure 57: TOF of Pt, Au, and MoS2 NFs in IL electrolyte (**a**) at small range of overpotentials (< 200 mV), (**b**) at high range of over-potential (> 700 mV). To explore the effect of solvents, a similar calculation method was also performed for MoS_2 NFs with different electrolytes i.e., IL, DMSO, and TGDME (Figure. 58a-b). These results also prove that MoS_2 NFs exhibit more than threefold higher TOFs inside the IL electrolyte compared to DMSO and TGDME at a low range of over-potentials. However at high over-potentials ~ an order of magnitude higher TOF was obtained in IL compared to two other electrolytes.



Figure 58: TOF of MoS_2 NFs at different electrolytes i.e., DMSO, TGDME and IL (**a**) at small range of over-potentials (< 200 mV), (**b**) at high range of over-potential (> 700 mV).

Therefore, based on the TOF results, recorded ORR and OER current densities, and the comparison with previously reported catalysts[35], [170]–[172] it can be safely claimed that MoS₂ NFs/IL is one of the most active systems for both ORR and OER.

To address the long term efficiency of our catalyst, we monitored the ORR and OER performance up to 750 CV cycles (~ 22 hrs) and performed elemental analysis afterward. Figure 59 shows the ORR current density trend at 2 V. Only 6.5% loss in ORR current density was observed after 750 continuous CV cycles, which could be due to a decrease in Li salt concentration as a result of Li consumption. This suggests a remarkably high stability of our catalyst.



Figure 59: Long-term performance analysis of MoS₂ NFs in ionic liquid. Only 6.5% loss in current density was observed after 750 cycles.

To do elemental analysis, X-ray photoelectron spectroscopy (XPS) experiments were performed using the Kratos Axis-165 instrument. The base pressure of the system was less than 2 x 10^{-10} Torr, while the pressure during analysis never exceeds 2 x 10^{-9} Torr[138].

Bulk MoS₂ samples were irradiated by a monochromatic Al-Ka X-ray source (15 kV, 10 mA). The angle of monochromatic light was fixed at 60 degrees with respect to the sample surface[138]. Photoelectrons were detected by 8 channeltrons of the concentric hemispherical analyzer over an area of 700 x 300 µm, with a spectrometer take-off angle of zero (with respect to the sample surface normal). The detection was achieved using the constant analyzer energy (CAE) mode [138]. Survey scans were acquired with a passenergy of 160 eV, 1.0 eV step-size and 100msec dwell time; while narrow scans were acquired with a pass-energy of 20 eV, 0.1 eV step-size and 200 msec. All scans were performed with the charge-neutralization system running[138]. Figure 60a shows the deconvoluted XPS spectra of MoS₂ (between 220 eV to 240 eV) before electrochemical experiment for Mo species. Data analysis show similar Mo^{IV}3d_{3/2}, Mo^{IV}3d_{5/2} and S2s peaks for both samples indicating that MoS₂ native elemental structure remain unchanged even after electrochemical experiments. The peak appearing at about ~233.2 eV and ~230.1 eV corresponds to the $3d_{3/2}$ and $3d_{5/2}$ respectively which is consistent with a +4 oxidation state for molybdenum. However, the S 2s peak typically isn't the most common peak for chemical-state determination arises at about 227.19 eV[138].

The X-ray photoelectron spectroscopy (XPS) experiments also performed on MoS_2 NFs before the and after 750 cycles (Figure 60b) also confirms the stability of our catalyst. The (XPS) spectrum of MoS_2 NFs obtained after 750 CV cycles consists of similar peaks with a small shift in the binding energy of the peak positions, which could be due to the presence of intercalated Li atoms or trivial variation in the MoS_2 phase state as reported

previously[175], [176]. Nevertheless, the intensity of the $Mo^{6+} 3d_{5/2}$ peak (~236.4 eV) remains low, confirming that MoS_2 NFs were not oxidized during ORR and OER cycles.



Figure 60: X-ray Photoelectron Spectroscopy (XPS) analysis of MoS₂ (a) before and (b) after 750 cycle CV experiment. XPS spectrum of MoS₂ atoms (for Mo) corresponds to the Mo $3d_{3/2}$ and Mo $3d_{5/2}$ which is consistent with a +4 oxidation state for Mo.

4.3. Performance of the MoS₂ NFs/IL cathode/electrolyte system in a Li-O₂ battery

In the above studies, we demonstrated high bi-functionality and long-term stability of the $MoS_2 NFs$ in a three-electrode electrochemical system. The next question is how the $MoS_2 NFs/IL$ cathode/electrolyte system performs in a Li-O₂ battery. To examine this, we assembled a Swagelok cell (Figure 61) comprised of 0.1 M LiTFSI in IL and a carbon free (without using Super P and binder) $MoS_2 NFs$ cathode. This allows us to avoid any effect of the Super P which is also known as an active catalyst for Li-O₂ battery system[177]. All battery experiments were performed in custom made Swagelok type battery set-up (Figure 61). This setup comprised of $MoS_2 NFs$ as a cathode, Aluminum mesh as both support and current collector, lithium chips as an anode and EMIM-BF4 electrolyte (HPLC grade,

Sigma Aldrich) with 0.1 M Lithium Bis(Trifluoromethanesulfonyl) Imide (LiTFSI) as a lithium salt (battery grade, Sigma Aldrich). The glassy carbon fiber was applied as a separator to avoid direct contact between cathode and anode. The 0.3 mg of MoS₂ NFs (dispersed in IPA) was coated layer by layer onto a 1.5 cm² gas diffusion layer (GDL) and dried inside a vacuum chamber at 120°C for 24 hrs to remove all impurities before transferring to Ar filled glove-box[60], [168], [178]. The battery set-up was assembled in an Ar filled glove-box and transferred to the sealed O₂ chamber for electrochemical measurements. In order to eliminate the effect of parasitic reactions, the chamber purged with pure O₂ to remove all gas impurities. The charging-discharging profile of assembled Li-air battery investigated by performing galvanometric experiments at constant current density (e.g., 0.1 mA.g⁻¹) to explore the electrochemical polarization gap. The battery capacity and cyclability examined by running charging-discharging experiments for different cycles (up to 50 cycles) at constant current rate.



Figure 61: Schematic diagram of custom made Swagelok cell for Li-O₂ battery

Figure 62 shows the discharging and charging profiles of this MoS_2 NFs/IL system as tested by capacity-limited (500 mAh.g⁻¹) cycling up to 50 cycles at the current density of 0.1 mA.cm⁻². The discharge (at the 1st cycle) begins at 2.90, and targeted discharge capacity (500 mAh.g⁻¹) was attained at potential 2.69 V. The charging process was also completed at a potential of 3.49 V.

The polarization gap is another key parameter for Li-O₂ batteries since the lower polarization gap results in higher round-trip energy efficiency. At 500 mAh.g⁻¹ capacity (normalized with MoS₂ mass), the polarization gap for the MoS₂/IL system is 0.8 V, which increases to 0.85 after 10 cycles. This is comparable with the gap of ~0.8 V reported for Au-Pt nanoparticle-based Li-O₂ batteries[33] tested at a current density of 0.04 mA.cm⁻² (compared to our 0.1 mA.cm⁻²). Moreover, the MoS₂/IL system is similar to that obtained for Pd nanoparticles deposited on Al₂O₃ passivated Super P carbon black[49]. For the same capacity (500 mAh.g⁻¹), the polarization gap for Pd based catalyst increases during 10 cycles from 0.55 to 0.9 V. The MoS₂ NFs/IL cathode/electrolyte system also has a lower polarization gap than that other systems such as TiC (1.25 V)[60] and metallic mesoporous pyrochlore (1.5 V)[179] based Li-O₂ batteries at their optimal experimental conditions.

Figure 62 also shows the variation in the discharging and charging potentials with respect to number of cycles. A small increment of the discharge (~20 mV) and charge potential (~ 120 mV) from the 2^{nd} cycle to the 50th cycle suggests a reversible formation/decomposition of ORR products and high stability of the MoS₂ NFs/IL system. Moreover, the discharge

capacity retention of the MoS_2/IL system based on a 2.7 V cut-off potential is ~8% between the 2nd and 50th cycles. This co-catalyst system also shows remarkably high round trip efficiency (~85%) for the 1st cycle, which drops slightly to ~80% after 50 cycles. The failure after 50 cycles is probably due to the corrosion of the lithium anode from O₂ crossover as the anode was black after 50 cycles[180].



Figure 62: Performance of bi-functional catalysts in Li-O₂ Swagelok battery. Charging and discharging voltage profiles of a battery using carbon free MoS_2 NFs and ionic liquid electrolyte saturated with 0.1 M LiTFSI as a Li salt. The discharge capacity retention of the same co-catalyst based on 2.7 V cut-off potential versus number of cycles (inset) shows ~ 8% decay between 2 to 50 cycles.

We also compared the MoS₂ NFs deeper discharge and charge performance with Au and Pt NPs at the same electrolyte (IL) (Figure 63). The deeper discharge followed by charge for our MoS₂ NFs/IL, Pt and Au NPs were performed using similar cell and experimental parameters (Figure 63). The charge–discharge test was carried out in potential-controlled mode. The lower potential's limits were 2.2 V for MoS₂ NFs/IL while Pt and Au NPs were studied up to 2.0 V discharge potential. However, the upper potential's limits was same

(4.0 V) for each system. The discharge process for $MoS_2 NFs$,/IL system takes two hours and thirty minutes to reach a discharging potential of 2.2 V and the calculated capacity was 1250 mAh.g⁻¹. The battery was fully recharged i.e., up to the similar capacity (~1250 mAh.g⁻¹) at 4.0 V charge potential for this system. However, Au and Pt NPs could only recharge 40% (~ 600 mAh.gr⁻¹) and 50% (~500 mAh.gr⁻¹) of their overall capacity (1450 and 1000 mAh.gr⁻¹ respectively). Moreover, at 500 mAh.gr⁻¹ capacity, approximately 1.0 V wider polarization gap has been observed for Au and Pt NPs compared to MoS₂ NFs system. Thus, our results indicate that the cell as reported in the paper is working at ~ 40% of its total capacity when we discharge to 2.2 V. Moreover, these results confirm bifunctionality of MoS₂ NFs compare to Au and Pt NPs at the same electrolyte (IL).



Figure 63: A deeper Discharge and charge profile of MoS_2 NFs, Au and Pt NPs in IL electrolyte with a discharge potential of 2.2 V for MoS_2 NFs and 2.0 V for Au and Pt NPs. The upper charge potential of 4 V was also applied for charge process. The discharge and charge curve is no longer completely flat under this deeper discharge and charge.

A charge and discharge experiment of MoS₂/DMSO were performed in the same custom made Swagelok cell under identical conditions. Our results clearly indicate that MoS₂/DMSO not only exhibits poor LSV performance but also this system shows poor

charging and discharging performance. A small capacity (~85 mAh.g⁻¹) was recorded under identical experimental conditions i.e., 0.1 mA.cm⁻² applied current density, with lower (1.0V) discharge and upper (5.0 V) charge potentials (Figure 64). The obtained capacity (~85 mAh.g⁻¹) is almost 15 times lower than that of observed for MoS₂/IL battery (~1250 mAh.g⁻¹) under the same conditions. The results are consistent with our CV experiments and DFT prediction (section 4.4) in that we have shown that Mo edge atoms get poisoned without using the ionic liquid.



Figure 64: Discharge and charge profile of MoS₂ NFs with DMSO electrolyte system.

In order to investigate the morphology of the discharge products in $MoS_2 NFs/IL$ system, we performed SEM of the cathode surface before and after the discharge process (Figure 65a and b).



Figure 65: (a) SEM images of discharged cathode and (b) SEM images of pristine cathode. These two images show the film-like along with some nanoparticle morphology for Li_2O_2 . Scale bars are 1 μ m.

The SEM images show film-like along with some nanoparticle morphology on the surface

(Figure. 66).



Figure 66: SEM images of discharged cathode. (**a-f**) The obtained SEM images show the film-like along with some nanoparticle morphology for Li_2O_2 . Scale bars are 1 µm for (a-d) and 500 nm for (e and d).

Energy-dispersive X-ray (EDX) O₂-phase image of a discharged cathode (Figure 67) further confirms the existence of oxygen enriched accumulated particles over the cathode surface.



Figure 67: Oxygen phase spectra and SEM image (inset). Scale bars are 2 µm.

Next, we performed differential electrochemical mass spectroscopy (DEMS) experiments particularly for the charging process and quantified the product[38], [181]. The experiments were performed using an HPR40 (Hiden Analytical) instrument consisting of a customized electrochemical cell. The customized DEMS electrochemical cell consists of a semi-permeable PTFE membrane (28 µm thick with a pore size of 20 nm) supported on Ni mesh to enrich the transition of gases and vapors. At first, a Swagelok battery cell consisting of MoS₂ NFs coated gas diffusion layer (GDL) as a cathode, a lithium chip as an anode, and a glass carbon fiber filter paper saturated in 0.1 M Lithium Bis(Trifluoromethanesulfonyl) Imide (LiTFSI) (battery grade, Sigma Aldrich) EMIM-BF4 electrolyte (HPLC grade, Sigma Aldrich) was integrated with the DEMS electrochemical cell. The discharging experiments were performed in an O₂ saturated

environment. In brief, the cell was discharged up to 500 mAh.g⁻¹ using 0.1 mA.cm⁻² current density while the O₂ (99.99% research grade) was continuously purged inside the cell. After an hour of the discharging process, the Swagelok battery integrated within the DEMS cell was flushed with Ar for 15 minutes to remove O₂ from the electrolyte and connected to the DEMS instrument. Prior to running charging experiments, the DEMS instrument was operated for long time (e.g., two hours) in order to make sure that all gas impurities were removed. The DEMS was operated in SEM (Secondary electron multiplier) detection mode as it offers higher sensitivity in comparison to Faraday detection mode. Hydrogen, O_2 and CO_2 signals remained constant prior to charging experiments. Next, we performed the charging cycle by applying 0.1 mA.cm⁻² current density and monitored the H₂, O₂ and CO₂ signals online continuously. We observed an immediate rise in the O₂ signal confirming the evolution of O₂ molecules as a result of discharge product decomposition. However, the SEM signals for H₂ and CO₂ remained unchanged. The results as shown in Figure 68 were constantly observed for the entire charging process until the maximum capacity (500 mAh.g⁻¹) was achieved.



Figure 68: DEMS profiles of the cell after 1^{st} , 20^{th} and 50^{th} cycles. DEMS data were collected during the charging process after the cell discharged up to 500 mAh.g⁻¹. DEMS experiment shows that O_2 gas is the only evolved gas during whole charging process.

In order to calculate the number of evolved O_2 molecules, we calibrated our DEMS system with 5, 10, 20 and 30% O_2 mixed with Argon. Our calculation shows that ~ 5×10⁻¹⁰ mole/s O_2 were evolved during charging process. Considering 0.1 mA applied current, the data indicates 2.04 electrons per O_2 . This verifies that Li₂ O_2 was a main discharge product. We also calculated the amount of Li₂ O_2 using the evolution rate of O_2 . Our calculation indicate that 83.8 µg Li₂ O_2 was produced during the discharge process, which is very close to its theoretical value (86 µg)[38], again confirming the Li₂ O_2 as the main discharge product. Moreover, we studied the cyclability of our battery cell by performing a similar DEMS experiment after 20 and 50 cycles as shown in the main text (Figure 68). The calculated charge-to-mass ratios (2e⁻/O₂ ratio) remain almost constant with a ± 4% variation with respect to the first cycle (Table 5). Interestingly, no CO₂ and H₂ evolution was observed even after 50 cycles.

Cycle #	evolved O ₂ (mole/s)	e⁻/O ₂ ratio	Li_2O_2 (µg)
1	5.07×10 ⁻¹⁰	2.04	83.8
20	5.14×10 ⁻¹⁰	2.01	84.9
50	4.98×10 ⁻¹⁰	2.08	82.3

Table 5. Properties of MoS₂ NFs/IL battery cell at different cycles.

We also performed Raman spectroscopy at the end of the 1st discharge cycle and 1st, 20th and 50th charge cycles to further study the stability and cyclability of the cell. Figure 69 shows the Raman spectrum of the cathode before and after discharging process normalized with the graphitic G band peak (Figure 70).



Figure 69: The Raman spectrum of cathode surface before and after discharge.

A new peak at 250 cm⁻¹ associated to the Li_2O_2 is clearly seen in the spectrum of the discharged cathode (Figure 69)[178], [182]. However, the second characteristic peak of Li_2O_2 at 788 cm⁻¹ interferes with a catalyst peak at the same position (Figure 70), but its intensity seen to be greater than that of undischarged cathode. Additionally, no peak was

observed for LiO₂ (1123 cm⁻¹) as an intermediate product, or Li₂CO₃ (1088 cm⁻¹) in the Raman experiment[183]. Similar results were obtained after the 20th and 50th charge cycles (Figure 71a-b).



Figure 70: Raman spectra of (a) discharged cathode, a peak at 250 cm⁻¹ associated to the Li_2O_2 was clearly seen in the spectrum of the discharged cathode. However, the second characteristic peak of Li_2O_2 at 788 cm⁻¹ interferes with catalyst peak at the same position. (b) Pristine cathode, the observed additional peaks mainly correlated to $MoS_2 NFs E_{2g}$ (inplane) and A_{1g} (out of plane) mode (blue line) and also some impurities (passivated in the vacuum chamber at 120°C for 24 hrs) which are believed to derive from liquid exfoliation process (black line). (c) GDL substrate, the graphitic D and G band peaks (inset) at 1334, and 1600 cm⁻¹ were also observed in all spectra.



Figure 71: Discharging/charging curve and corresponding Raman spectra of cathode (a) after 1^{st} cycle discharge (b) after 1^{st} , 20^{th} and 50^{th} charging cycles. The absence of Li₂O₂ characteristic peak at 250 cm⁻¹ and the intensity decrease at 788 cm⁻¹ after 1^{st} , 20^{th} and 50^{th} charging cycles can also be correlated to Li₂O₂ decomposition.

X-ray diffraction (XRD) analyses of a pristine and discharged cathode surface were also

carried out to further clarify the crystal structure of the product (Figure 72).



Figure 72: XRD analysis of the discharged cathode before and after discharge process.

The XRD spectrum exhibits sharp peaks at 33° , 35° , 49° and 58° which correspond to the (100), (101), (103) and (110) crystal surfaces of Li₂O₂, respectively. The peaks completely

disappeared after the 1st charge cycle. These results were also repeated for the 20th and 50th cycles (Figure 73) further confirming; (i) the Li_2O_2 formation and its complete decomposition as the main discharge product[60], [168], [178], and (ii) the high cyclability and stability of the cell after 50 cycles.



Figure 73: XRD spectra of cathode (a) after 1st cycle discharge and charge, **(b)** after 20th and 50th charging cycles.

4.4. Density functional calculations

We performed density functional theory (DFT) calculations to provide a mechanistic understanding of the MoS_2/IL system during discharge. Previous studies have suggested that the first step in the discharge product formation for Li-O₂ batteries involves the oxygen reduction at the cathode[182], [184]:

$$O_2 + * \rightarrow O_2^*$$
 (cathode) (1)

$$e^- + O_2^* \rightarrow O_2^{-*}$$
 (cathode) (2)

where the initial reaction on the cathode is O_2 binding onto the surface of the electrode followed by reduction to form an adsorbed species O_2^{-*} (Eqn. 1). There are various possible reaction steps that can occur following oxygen reduction. One scenario[185] is that the initial oxygen reduction is followed by reaction with Li⁺ cations and another electron transfer all occurring on the cathode surface with resulting growth of Li₂O₂. Another scenario[178], [186], [187] is based on a through-solution mechanism where the O_2^{-} desorbs into the electrolyte and solution phase reactions result in the discharge product formation. In this scenario Li₂O₂ can form by disproportionation (Eqn. 3) of LiO₂ either in solution or on the surface.

$$2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2 \qquad (3)$$

The formation of O_2^{-*} (reactions (1) and (2)) is key to determining the rate at which oxygen reduction occurs and thus the efficiency of the discharge process. Therefore, in this computational study we have focused on O_2^{-*} formation on the MoS₂ NFs using DMSO and IL as electrolytes to provide insight into the experimental results.

The reaction pathways of O_2 adsorption on MoS_2 NFs in presence of the DMSO and IL are shown in Figure 74. As shown in this figure, in the DMSO electrolyte adsorption of an O_2 molecule onto the exposed Mo edge of MoS_2 flake (modeled as a MoS_2 nanoribbon) leads to the direct dissociation of the O_2 molecule to form two bound O atoms on the Mo edge, with no barrier (Figure 74, state 5 or 6). This dissociative adsorption reaction is highly favorable, with a calculated adsorption energy of -8.0 eV. Based on the calculations, continued dissociation of O_2 molecules would occur on the Mo edge, and ultimately lead to a fully oxidized Mo edge (Figure 74, state 8). A highly stable, fully oxidized Mo edge will not bind additional O_2 molecules and, therefore, will not be very favorable for oxygen reduction. However, in some cases, where the Mo edge is only partially oxidized, the Mo edge can bind to additional O_2 molecules (Figure 74, state 6), forming O_2^{-*} with charge transfer (Figure 74, state 7). Nevertheless, the thermodynamics will drive the reaction toward full oxidation of the Mo edge and poison the catalyst (Figure 74, state 8).

On the other hand, using an ionic liquid as the electrolyte can effectively prevent O_2 from dissociating on the electrode (Figure 74, state 1 to 3). Previously, both computational and experimental studies have shown that ionic liquid ions exhibit strong attractive interactions with an electrode surface under electrochemical conditions[188]. In general, the cations of ionic liquids are attracted by the cathodes, while the anions are attracted by the anodes. In the present DFT studies, the (EMIM⁺ + e⁻) pairs were added to the Mo edge to mimic the electrochemical adsorption of EMIM⁺ on a MoS₂ electrode, and to keep the calculated systems neutral. The DFT calculations showed that the EMIM⁺ ions are likely to bind to the MoS₂ flakes with the EMIM⁺ ring parallel to the Mo edge, and each EMIM⁺ ion binds to two Mo atoms. The calculated density of states shows strong interactions between an EMIM⁺ ion and the Mo edge with the presence of an extra electron, which favors the Mo edge being largely covered by the EMIM⁺ ions during the discharge process. Due to randomness of adsorption process and steric repulsion of neighboring EMIM⁺ ions on the edge, gaps in the EMIM⁺ coverage result in isolated Mo atoms exposed on the edge. For O_2 dissociation to occur, however, each O_2 molecule requires at least two nearby Mo atoms. The isolated Mo sites (Figure 74, state 2) would only lead to O_2 binding with no dissociation (Figure 74, state 3), which forms O_2^{-*} . Based on these calculations, the strong electrostatic interaction between the ionic liquid (EMIM⁺ ions) and the MoS₂ flakes tend to prevent complete O_2 dissociation on the Mo edge, and lead to the formation of oxygen reduction sites, O_2^{-*} .



Figure 74: Illustration of the oxygen reduction reaction (ORR) on MoS₂ NFs in two different electrolytes (ionic liquid ([EMIM][BF4]) and DMSO) based on DFT calculations. In the ionic liquid electrolyte, EMIM⁺ molecules bind strongly to the negative charged Mo edge (state 1) and form EMIM⁺ covered Mo edge, leaving singleatom Mo sites exposed to the solvent (state 2). Then O₂ binds onto the single-atom Mo sites and with charge transfer forms O₂⁻ (state 3). However, in DMSO electrolyte, the neutral DMSO molecules only binds weakly to the Mo edge (state 4), and leaves multiatom Mo sites exposed to the solvent. An O₂ molecule can either replace an adsorbed DMSO molecule on the Mo edge or bind directly on the multi-atom Mo sites, and rapidly dissociate to two bound O atoms on the Mo edge (state 5). In some cases, the dissociated

O atoms may rearrange on the Mo edge, and form an active binding site (state 6), and O_2 can be reduced to O_2^- on this site (state 7). However, continued O_2 dissociation on the Mo edge is thermodynamically favorable and will eventually lead to a highly stable oxidized Mo edge (state 8), which is deactivated. (The numbers in the figures are reaction energies, eV)

Following the formation of O₂^{-*}, the mechanism of the Li₂O₂ formation in the EMIM-BF₄ electrolyte was investigated. In our Li-O₂ battery based on MoS₂/IL the first scenario mentioned above, i.e., the surface growth mechanism, is not likely. The reason is that the catalyst active sites, the Mo edge atoms of the MoS_2 nanoflakes, would be blocked and deactivated by the growth of bulk Li_2O_2 , which is very unlikely due to the excellent performance of the cell. On the other hand, the second scenario, i.e., the through-solution mechanism, is likely since it does not necessarily block catalytic sites. Thus, some of the steps in the second scenario were investigated with DFT calculations; other aspects such as nuclearion and growth are beyond the scope of this study. The O_2^- superoxide anion is calculated to be stabilized in EMIM-BF₄ by a large solvation energy (3.03 eV). This is also consistent with a high Gutman accepter number (AN) for EMIM-BF₄ (33.5), which indicates a high stability for O_2^- in the IL solution [178]. Therefore, after O_2^- is formed on the catalyst active site, it can desorb into the EMIM-BF₄ electrolyte due to the strong solvation effect. The next step is the formation of solvated LiO₂ from solvated Li⁺ and O₂⁻ $(Li^+ + O_2^- \rightarrow LiO_2, Eq (4))$ in the IL, which is calculated to be thermodynamically favorable with a reaction free energy of -2.49 eV. Then, two solvated LiO₂ molecules can form an $(LiO_2)_2$ dimer, with a dimerization energy of -0.48 eV (Figure 75). The $(LiO_2)_2$ dimer can disproportionate to form Li_2O_2 with a small barrier of 0.25 eV (Figure 75). Because Li_2O_2 is not highly soluble, it is likely that Li_2O_2 then deposits by nucleation and growth on the electrode and further crystallizes[186]. The DEMS results discussed above confirm that Li_2O_2 is the main product, which is consistent with the discharge mechanism modeled by our DFT calculations.



Figure 75: Calculated reaction mechanism of the formation of Li_2O_2 in EMIM-BF₄ electrolyte (Reaction free energies, eV). LiO_2 is formed through IL solution by the interaction of dissolved Li^+ and O_2^- . Li_2O_2 is formed through the disproportionation of LiO_2 in IL.

Thus, we propose that the MoS_2/IL combination acts as a co-catalyst whereby the IL promotes the catalytic properties of the MoS_2 NFs by preventing oxidation of the edges and facilitating the dissolution of O_2^- . The formation of Li_2O_2 is likely to undergo a through solution mechanism in this system. The poorer performance of the aprotic electrolytes, DMSO and TEGDME, confirms the synergistic effect predicted by theory for the MoS_2/IL combination.

4.5. Summary and conclusion

In summary, this study has demonstrated that a cathode based on molybdenum disulfide (MoS_2) nanoflakes combined with the ionic liquid EMIM-BF₄ work together as an effective co-catalyst for discharge and charge in a Li-O₂ battery. Cyclic voltammetry results show superior reaction rates for this co-catalyst at lower overpotentials for oxygen reduction and evolution reactions compared to Au and Pt metal catalysts under identical experimental conditions. This MoS₂/IL co-catalyst also performs remarkably well in Li-O2 battery system with a small discharge/charge polarization gap as well as good stability and cyclability. Atomic scale characterizations (STEM and EELS experiments) and DFT calculations were used to elucidate the mechanism by which the MoS_2 and the ionic liquid electrolyte act together to promote the catalytic properties of the MoS_2 . It was shown that the coverage of the Mo edge by the EMIM⁺ ions tend to form isolated Mo sites, which prevent O₂ dissociation and enable oxygen reduction. In addition, IL facilitates the dissolution of O_2^- , which leads to the formation of Li_2O_2 via a through solution mechanism. The MoS₂/IL co-catalyst discovered in this work provides new opportunities for exploiting the unique properties ionic liquids such as their stability in Li-air batteries as well as activity of MoS₂ as a cathode material.

5. CHAPTER 5: Conclusion and Future proposed work

In conclusion, we have shown that the inexpensive non noble metal transition metal dichalcogenide (TMDC) catalysts can open up a new route for development of highly active catalysts in a variety of electro and photo electrochemical applications. We have discovered that the electronic structure of the TMDCs family catalyst is well suited to any electro- and photo-electrochemical applications due to the higher density of d-orbital electrons near the fermi level of energy and low work function compared to other commonly used catalysts. This performance is also boosted by using an appropriate electrolyte, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄), which can enhance the catalytic performance by facilitating the reaction.

In particular, we have demonstrated that TMDC NFs in the ionic liquid EMIM-BF₄ work as the most effective catalysts for CO₂ reduction. Cyclic voltammetry results show superior reaction rates for the WSe₂ NF catalyst among all other TMDC NFs (MoS₂, WS₂ and MoSe₂) under identical experimental conditions. The WSe₂ NFs also perform extremely well compared with common noble metal catalysts (e.g., Ag and Au) with two to three orders of magnitude higher activity at low overpotentials. Atomic scale characterizations (STEM) and DFT calculations were used to elucidate electronic and catalytic properties of TMDCs, suggesting that the exposed metal edge sites (Mo and W) are contributing to high activity.

We also showed that a cathode based on molybdenum disulfide (MoS₂) nanoflakes combined with the ionic liquid EMIM-BF4 works as an effective co-catalyst system for discharge and charge in a Li-O₂ battery. Cyclic voltammetry results show superior reaction rates for this co-catalyst at lower overpotentials for oxygen reduction and evolution reactions compared to Au and Pt metal catalysts under identical experimental conditions. This MoS₂/IL co-catalyst also performs remarkably well in a Li-O₂ battery system with a small discharge/charge polarization gap as well as good stability and cyclability. Atomic scale characterizations (STEM and EELS experiments) and DFT calculations were used to elucidate the mechanism by which the MoS₂ and the ionic liquid electrolyte act together to promote the catalytic properties of the MoS_2 . It was shown that the coverage of the Mo edge by the EMIM⁺ ions tends to form isolated Mo sites, which prevent O₂ dissociation and enable oxygen reduction. In addition, the IL facilitates the dissolution of O_2^- , which leads to the formation of Li_2O_2 via a through solution mechanism. The MoS₂/IL co-catalyst discovered in this work provides new opportunities for exploiting the unique properties of ionic liquids such as their stability in Li-air batteries as well as activity of MoS₂ as a cathode material.

In the future, we are interested in continuing the work in two separate phases: (i) study the electrochemical and photo-electrochemical performance of promoted TMDCs by boosting the electronic properties of their host atoms, aiming to further improve the performance of the CO_2 reduction reaction; (ii) study the performance of the hybrid structure of TMDCs consisting of similar atomic arrangement but different electronic properties to enhance the performance of the Li-O_2 battery in comparison to the MoS_2 nanoflakes.

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APPENDIXES

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For chapter 3 (reference 2):



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Patents:

- 1. Transition Metal Dichalcogenides (TMDCs) Based Catalysts for CO₂ Reduction, Amin Salehi-Khojin, M. Asadi, B. Kumar, US Patent Application # 61/840,167.
- Novel Catalyst System for Advanced Metal-Air Batteries, Amin Salehi-Khojin, M. Asadi, B. Kumar, Submitted, *Provisional Patent Applcation*, UIC Technology No.: DH071.
- 3. Artificial Leaves for Energy Applications, Amin Salehi-Khojin, M. Asadi, B. Kumar, *Provisional Patent Applcation*, UIC Technology No.: DH167.
- 4. **3D structured Molybdenum Disulfide for Energy Related Applications,** Amin Salehi-Khojin, Amirhossein Behranginia, **M. Asadi**, *disclosure form*.
- 5. Humidity Sensing in Black Phosphorus Thin Films, Amin Salehi-Khojin, Poya Yasaei, Amirhossein Behranginia, M. Asadi, *disclosure form*.

Journal papers:

 Jun Lu*, Yun Jung Lee*, Xiangyi Luo*, Kah Chun Lau*, Mohammad Asadi*, Hsien-Hau Wang*, Jianguo Wen, Dengyun Zhai, Dean Miller, Yo-Sub Jeong, Jin-Bum Park, Zhigang Zak Fang, Bijandra Kumar, Amin Salehi-Khojin, Yang-Kook Sun, Larry A. Curtiss, Khalil Amine, "A Lithium-Oxygen Battery Based on Lithium Superoxide" Nature, 2015, Accepted.

- 2. Mohammad Asadi^{*}, Bijandra Kumar^{*}, Patrick Phillips, Robert F. Klie, Larry A. Curtiss, Amin Salehi-Khojin '' A Cathode Based on Molybdenum Disulfide nanoflakes for Lithium–Oxygen Batteries'' *ACS nano*, 2015, under review.
- 3. Mohammad Asadi, Kibum Kim, Cong Liu, Venkata Aditya Addepalli, Poya Yasaei, Patrick Phillips, Amirhossein Behranginia, Pedram Abbasi, Richard Haasch, Peter Zapol, Bijandra Kumar, Robert F. Klie, Jeremiah Abiade, Larry A. Curtiss, Amin Salehi-Khojin'' Transition metal dichalcogenides as highly active electrocatalysts for carbon dioxide reduction'' *Science*, 2015, under in-depth review.
- 4. Amirhossein Behranginia*, Mohammad Asadi*, Poya Yasaei, Bijandra Kumar, Patrick Phillips, Tara Foroozan, Joseph C. Waranius, Pengcheng Sun, Jeremiah Abiade, Robert F. Klie, Amin Salehi-Khojin, "Highly Crystalline Layered Three Dimensional Molybdenum Disulfides for Electro-catalytic Applications" Chemistry of Materials, 2015, under in-depth review.
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- Mohammad Asadi*, Bijandra Kumar*, Amirhossein Behranginia, Brian A. Rosen, Artem Baskin, Nikita Repnin, Davide Pisasale, Patrick Phillips, Wei Zhu, Richard Haasch, Robert F. Klie, Petr Král, Jeremiah Abiade, Amin Salehi-Khojin, "Robust carbon dioxide reduction on molybdenum disulphide edges" Nature Communications 5, (2014).

<u>Also highlighted in more than 200 news coverage (e.g. Science Magazine, NERSC/Berkeley Lab, Science Daily, Yahoo News, NSF etc).</u>

- Bijandra Kumar*, Mohammad Asadi*, Davide Pisasale, Suman Sinha-Ray, Brian A. Rosen, Richard Haasch, Jeremiah Abiade, Alexander L. Yarin, Amin Salehi-Khojin "Renewable, Metal Free and Non-precious Carbon Nanofiber Catalysts For CO₂ Conversion" Nature Communications 4,(2013). <u>Also highlighted in more than 100 news magazine (e.g. MIT Technology Review, Science Daily, Nanowerk, Phy.org etc).</u>
- Mohammad Asadi, Ebrahim Alaei, Jalal Shayegan, "Photo-catalytic Degradation of Polynuclear Aromatic Hydrocarbons Contaminated Soils in South Pars Economic and Energy Zone with TiO₂ Nano-catalyst" Iranian Journal of Chemical Engineering (IJChE), Volume 4, Number 1 (winter), P14-20, 2007.

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Conference Proceedings:

- 1. Amirhossein Behranginia, Mohammad Asadi, Amin Salehi-Khojin, "**Three Dimensional Molybdenum Disulfides Grown on Monolayer Graphene for Hydrogen Evolution Reaction**" Material Research Society (MRS), Boston, MA, Fall 2015.
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- Mohammad Asadi, Bijandra Kumar, Amirhossein Behranginia, Amin Salehi-Khojin, "Electrochemical Reduction of Carbon Dioxide on Molybdenum Disulfide Edges" American Institute of Chemical Engineers (AIChE) Annual Meeting, Atlanta, GA, November 2014.
- 4. Bijandra Kumar, Mohammad Asadi, Amin Salehi-Khojin, **''Hetero-Atomic Carbon Nanostructures for Carbon Dioxide Reduction''** AIChE Annual Meeting, Atlanta, GA, November 2014.

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