# THE BASAL PLANE ACTIVATION IN MONOLAYER MOLYBDENUM DISULFIDE FOR CARBON DIOXIDE REDUCTION VIA INTRINSIC DEFECTS

A thesis

Submitted to

McGill University

In Partial Fulfillment

of the Requirements of the Degree of

Master of Science

by

Ying Zhao

Department of Materials Engineering

McGill University, Montreal



October 2021

© Ying Zhao 2021

#### ABSTRACT

The growing concentration of atmospheric carbon dioxide (CO<sub>2</sub>) has become one of the biggest environmental and social concerns in recent years. The choice and tailoring of material are essential to efficiently reducing CO<sub>2</sub>. Two-dimensional (2D) materials have attracted enormous scientific interest in electrocatalysis due to their unique structural and electronic properties. Molybdenum disulfide (MoS<sub>2</sub>), a typical member of the 2D Transition Metal Dichalcogenide (TMDC) family, has recently arisen as a potential candidate promising high catalytic activities for a wide range of chemical reactions. However, pristine  $MoS_2$  suffers from a bottleneck of it being active only at edge sites. Exploring ways to render  $MoS_2$  catalytically active at locations beyond its edges is needed to subdue this problem. In this thesis, focusing on polycrystalline  $MoS_2$  for catalyzing CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), we have performed systematic studies to investigate the role of grain boundaries (GBs) on the catalytic performance of MoS<sub>2</sub> for CO<sub>2</sub> reduction. Bicrystalline MoS<sub>2</sub> sheets containing different GBs have been constructed, and the catalytic performance of CO<sub>2</sub>RR has been examined. Our results show that most GBs can contribute to lowering the energy barrier of CO<sub>2</sub>RR. This effect can be further amplified with the introduction of vacancies. With GBs decorated by single vacancies, the energies of potential-determining steps of CO<sub>2</sub>RR are further reduced, thus providing even more enhancement of the catalytic activities. In addition, GBs and vacancies can break the scaling relations between reaction intermediates, which is crucial in improving catalytic efficiencies. Our findings demonstrate that GB engineering can be an effective way to activate the basal plane of MoS<sub>2</sub> for CO<sub>2</sub>RR, providing valuable insights towards engineering MoS<sub>2</sub> for high-performing CO<sub>2</sub>RR electrocatalysts.

#### RÉSUMÉ

La concentration croissante de dioxyde de carbone (CO<sub>2</sub>) dans l'atmosphère est devenue l'une des plus grandes préoccupations environnementales et sociales de ces dernières années. Le choix et l'adaptation du matériau sont essentiels pour réduire efficacement le CO<sub>2</sub>. Les matériaux bidimensionnels (2D) ont suscité un énorme intérêt scientifique pour l'électrocatalyse en raison de leurs propriétés structurelles et électroniques uniques. Le bisulfure de molybdène (MoS<sub>2</sub>), un membre typique de la famille des dichalcogénures de métaux de transition 2D (TMDC), est récemment apparu comme un candidat potentiel prometteur d'activités catalytiques élevées pour un large éventail de réactions chimiques. Cependant, le MoS<sub>2</sub> vierge souffre d'un goulot d'étranglement car il n'est actif que sur les sites périphériques. Pour résoudre ce problème, il est nécessaire d'explorer des moyens de rendre le  $MoS_2$  catalytiquement actif à des emplacements audelà de ses bords. Dans cette thèse, en se concentrant sur le  $MoS_2$  polycristallin pour catalyser la réaction de réduction du CO<sub>2</sub> (CO<sub>2</sub>RR), nous avons réalisé des études systématiques pour étudier le rôle des joints de grains (GB) sur les performances catalytiques du MoS<sub>2</sub> pour la réduction du CO<sub>2</sub>. Des feuilles de MoS<sub>2</sub> bicristallin contenant différents GB ont été construites et les performances catalytiques du CO<sub>2</sub>RR ont été examinées. Nos résultats montrent que la plupart des GB peuvent contribuer à abaisser la barrière énergétique du CO<sub>2</sub>RR. Cet effet peut être encore amplifié avec l'introduction de postes vacants. Avec des GB décorés par des lacunes uniques, les énergies des étapes de détermination du potentiel du CO<sub>2</sub>RR sont encore réduites, offrant ainsi une amélioration encore plus importante des activités catalytiques. Les GB et les lacunes se sont révélés capables de briser les relations d'échelle entre les intermédiaires de réaction, ce qui est crucial pour améliorer l'efficacité catalytique. Nos résultats démontrent que l'ingénierie GB peut être un moyen efficace d'activer le plan basal du MoS<sub>2</sub> pour le CO<sub>2</sub>RR, fournissant des

informations précieuses sur l'ingénierie du MoS<sub>2</sub> pour les électrocatalyseurs CO<sub>2</sub>RR hautes performances.

## TABLE OF CONTENTS

Table of Contents iv
List of Figures
List of Tables
1. Introduction
2. Literature Review
2.1 Reaction Mechanisms of Electrochemical CO <sub>2</sub> RR
2.2 TMDCs for $CO_2RR$
2.3 2D Materials Design for CO <sub>2</sub> RR
2.4 Challenges and Research Needs of 2D Materials for CO <sub>2</sub> RR
3. Methodology
3.1 Model Construction
3.2 Computational Details
3.3 Calculation Methodologies
3.3.1 Formation Energies of MoS <sub>2</sub> GBs
3.3.2 Formation Energy of Vacancies
3.3.3 Gibbs Free Energy
3.3.4 Electronic Properties
4. Research Findings and Discussion
4.1 Formation Energies of GBs

4.2	Gibbs Free Energy	. 27
4.3	Scaling Relations	. 31
4.4	Electronic Properties	. 32
5. Co	onclusion	. 39
5.1	Summary of Research	. 39
5.2	Recommendations for Further Research	. 40
5.3	Significance of the Study	. 40

## LIST OF FIGURES

Figure 2-1. Different types of 2D materials [79]
Figure 2-2. Relation between number of carbons in the CO <sub>2</sub> RR product and the steps required to
reach the product [87]9
Figure 2-3. Pathways for CO <sub>2</sub> RR into C1 and C2 products [81]9
Figure 2-4. Top and side views of TMDCs [88] 10
Figure 2-5. (A) Different Nb-doped $MoS_2$ structures, (B) Gibbs free energy changes for the
reaction steps form CO <sub>2</sub> to CO, and (C) the energies required for COOH adsorption and CO
desorption [30]
Figure 2-6. Scaling relationships between (left) *COOH and (right) *COH and CO for transition-
metal doped $MoS_2$ (edges), bare metal 111 surfaces, and bare metal 211 surfaces [56]12
Figure 2-7. Binding energies of (a) COOH* and (b) CHO* vs. CO* on group X TMDs with
different number of vacancies. (c) Binding energies of H and OH on PtS <sub>2</sub> and PtSe <sub>2</sub> with varying
percentage of vacancies [57] 13
Figure 2-8. D-band model illustrating bond formation at a transition-metal surface [91]
Figure 2-9 .(A) Free energy diagrams for CO <sub>2</sub> reduction to CO on different surfaces. Partial
density of states of (B) the surface Ag55 atom and (C) edge W atom of the WSe <sub>2</sub> nanoflakes
[23]15
Figure 2-10. ensity of states diagrams, cross-sectional views of charge density isosurfaces, and
crystal structures for (A)(B)(C) MoSeS, (D)(E)(F) MoS <sub>2</sub> , and (G)(H)(I) MoSe <sub>2</sub> [54]16
Figure 2-11. Limiting potential of the *CO to *CHO formation step [56] 17
Figure 2-12. Binding configurations of CO* and CHO* on the edge of Ni-doped MoS <sub>2</sub> [56] 17

Figure 3-1. (a) The top and side views of pristine $MoS_2$ with AC edges and ZZ edges, and the top
views of the relaxed configurations of (b) 5 7a, (c) 5 7b, (d) 4 8a, (e) 4 8b, (f) 8 8a, (g) 8 8b, and
(h)4 4 GBs, where Mo atoms are shown in purple and S atoms are shown in yellow 20
Figure 3-2. Quantum dot constructions for (a) n=5 and (b) n=11, where Mo atoms are shown in
purple and S atoms are shown in yellow
Figure 4-1. Formation energies of the GBs as functions of the chemical potential of S, $\mu_S$ 27
Figure 4-2. (a) Energetics of the $CO_2RR$ process on different $MoS_2$ GBs (b) Energetics of the
CO <sub>2</sub> RR process on different MoS <sub>2</sub> SV GBs
Figure 4-3. (a) Relationship between $\Delta E$ and C-S bond length of COOH adsorption on clean
GBs. (b) Side view of COOH adsorption on 4 8b GB, with color label below the figure
Figure 4-4. The side view of CO adsorptions on (a)4 8a, (b)5 7b, and (c)4 4 GBs, with CO
lengths labeled
Figure 4-5. Top view of COOH (a and c) and CO (b and d) adsorption on the pristine (a and b)
and defective (c and d) 4 4 GBs
Figure 4-6. Binding energy relationships between $E_b(COOH)$ and $E_b(CO)$ for different GBs with
and without vacancies. The dotted line approximates the scaling relation of SV GBs. The grey
area represents CO physisorption, and the blue area represents CO chemisorption. Magnified top
view of COOH and CO adsorptions on 8 8b and 4 8b SV GBs are shown on the left and right
side of the figure, respectively
Figure 4-7. Relationship between p-band center and COOH adsorption energy on pristine GBs.
Figure 4-8. DOS plots for (a) pristine MoS2 and (b) 5/7b GB (top panel) before adsorption,
(middle panel) after COOH adsorption, and (bottom panel) after CO adsorption

Figure 4-9. Number of excess charges on (a) COOH with and without single S vacancies on
different GBs, and (b) CO for chemisorption cases, with respect to adsorption energies. Blue and
pink shadows highlight the GB and vacancy added GB systems, respectively
Figure 4-10. Top and side views of charge distributions for CO adsorptions on (a) 5 7b and
(b)4 8a GBs. The yellow region represents the negative charge density difference of $-0.005$ e
Bohr <sup><math>-1</math></sup> , and the cyan region represents the positive charge density difference of +0.005 e Bohr <sup><math>-1</math></sup> .
Figure 4-11. DOS plots for 4 8a GB (top panel) and 5 7b GB (bottom panel) after CO adsorption.

Figure S1. Energies of 5 7b structures with different edge separation distances (i.e., vacuum
distances between adjacent edges)
Figure S2. Linear fitting of f with respect to n
Figure S3. The COOH adsorption configurations for (a) basal, (b) 5 7a, (c)5 7b, (d)4 8a, (e) 4 8b,
and (f) 8 8b GBs
Figure S4. The CO adsorption configurations for (a) basal, (b) 5 7a, (c)5 7b, (d)4 8a, (e) 4 8b, and
(f) 8 8b GBs
Figure S5. The COOH adsorption configurations for (a) basal, (b) 5 7a, (c)5 7b, (d)4 8a, (e) 4 8b,
and (f) 8 8b GB <sub>SV</sub>
Figure S6. The CO adsorption configurations for (a) basal, (b) 5 7a, (c)5 7b, (d)4 8a, (e) 4 8b, and
(f) 8 8b GB <sub>SV</sub>
Figure S7. Charge distribution for COOH adsorptions on (a) basal, (b) 4 4, (c) 5 7a, (d)5 7b,
(e)4 8a, (f) 4 8b, and (g) 8 8b GBs

Figure S8. Charge distribution for CO adsorptions on (a) basal, (b) 4 4, (c) 5 7a, (d) 4 8b, and (d)	e)
8 8b GBs	51
Figure S9. Charge distribution for COOH adsorptions on (a) basal, (b) 4 4, (c) 5 7a, (d)5 7b,	
(e)4 8a, (f) 4 8b, and (g) 8 8b GB <sub>SV</sub>	52
Figure S10. Charge distribution for CO adsorptions on (a) basal, (b) 4 4, (c) 5 7a, (d)5 7b, (e)4	8a,
(f) 4 8b, and (g) 8 8b GB <sub>SV</sub>	53
Figure S11. Competing HER free energies for GB <sub>SV</sub> systems.	54

## LIST OF TABLES

Table 2-1. Main C1 products of CO <sub>2</sub> RR and reactions related to CO <sub>2</sub> RR [80]	. 7
Table 4-1. Carbon ligancy numbers for CO adsorptions on different GBs (with vacancy) with	
respect to the CO binding energies	36

Table S1. Free energy corrections ( $\Delta E_{corr}$ ) for non-adsorbed species	42
Table S2. Free energy corrections ( $\Delta$ Ecorr) for adsorbed species on different GBs	42
Table S3. Free energy change of each configuration for step 1	45
Table S4. Free energy change of each configuration for step 2	46
Table S5. Free energy change of each configuration for step 3	47
Table S6. Vacancy formation energies for different GB structures	48
Table S7. P-band center for COOH adsorption on pristine GBs	48
Table S8. Charges around absorbates after adsorptions	49

#### ACKNOWLEDGEMENTS

I would first like to express my deepest gratitude to my supervisor, **Professor Jun Song**, for allowing me to pursue research in his team, for his genuine professional and financial support throughout my master's study, as well as for being an incredible mentor and role model. I am also thankful for the help of **Pengfei Ou** and **Yiqing Chen** for their professional guidance and advice on my studies and research. I would also like to acknowledge my committee member, **Professor Jinhyuk Lee**, for his valuable time and suggestions on my research.

I would also like to acknowledge Compute Canada and Calcul Quebec for using their clusters for computations.

Last but not least, I am forever grateful to my parents. They have been supporting every decision that I have made and being there for me no matter what. I am very grateful for their support throughout this project.

## **DEDICATION**

To my beloved mom and dad

for always understanding me,

supporting me,

encouraging me,

and inspiring me to pursue my dream.

#### **1. INTRODUCTION**

Carbon dioxide (CO<sub>2</sub>) is the primary greenhouse gas emitted through human activities such as fossil fuel consumption. Its increasing atmospheric concentration drives global climate change and has therefore become a significant concern in modern society. In recent years, there have been notable efforts for mitigating the effect of CO<sub>2</sub> emissions on climate. Among various methods [1], electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) has received considerable attention, mainly because it represents an appealing route to reduces CO<sub>2</sub> into clean and sustainable chemical fuels under ambient conditions [2-7].

One of the most critical and acknowledged routes for CO<sub>2</sub>RR is the reverse-water gas shift (CO<sub>2</sub> +H<sub>2</sub>  $\leftrightarrow$  CO + H<sub>2</sub>O). Currently, noble metals such as gold (Au) [8-10], copper (Cu) [11-14], silver (Ag) [15, 16], and palladium (Pd) [17-19] are regarded as the best electrocatalysts for this process in terms of the selectivity of products [20]. However, these materials greatly suffer from their high costs, which impede their large-scale applications. Therefore, it is crucial to seek efficient and affordable alternatives to metallic electrocatalysts for CO<sub>2</sub>RR.

Two-dimensional (2D) materials such as graphene, transition metal dichalcogenides (TMDCs), and black phosphorus have attracted enormous scientific interest in catalysis due to their unique properties. Among these 2D materials, TMDCs have received much attention due to their unique electrical, mechanical, and optical properties, which can make up for some shortcomings of other materials [21, 22]. Asadi et al. found that the formation of CO\* from CO<sub>2</sub> is more favorable on the edges of TMDC nanoflakes than on bulk Ag, where the edge of tungsten diselenide (WSe<sub>2</sub>) obtained a high current density of 18.95mA/cm<sup>2</sup> at a low overpotential of 54mV [23]. Among all types of TMDCs, molybdenum disulfide (MoS<sub>2</sub>), a

typical member of 2D TMDCs, has been commonly studied as catalysts for a wide range of chemical reactions involving CO<sub>2</sub>RR [24-28]. For instance, Asadi et al. reported that MoS2 with Mo-terminated edges could catalyze CO<sub>2</sub>RR at a high current density (130mA/cm<sup>2</sup>) and a low overpotential (54mV)[29]. Abbasi et al. discovered that the required overpotential could be further lowered to 31mV by doping at the edges of MoS<sub>2</sub> [30]. Li et al. found that the edge-exposed 2H MoS<sub>2</sub> hybridized with N-doped carbon could expose a large number of active sites, which led to lower energy required for the potential limiting step of CO<sub>2</sub>RR (0.46eV) compared to MoS<sub>2</sub> edge (0.51 eV) and basal plane (2.47 eV) [31]. However, like most TMDCs, the active catalytic sites of MoS<sub>2</sub> are limited to the exposed edges, while the large area of the basal plane is catalytically inert. This inert area substantially limits the applications of MoS<sub>2</sub> as CO<sub>2</sub>RR

Chemical vapor deposition (CVD), the widely accepted fabrication method for TMDCs, often results in oriented crystal domains, indicating virtually inevitable formations of grain boundaries (GBs) [32]. Suppose GBs alone can activate the basal plane of MoS<sub>2</sub> for CO<sub>2</sub>RR with great catalytic performances. In that case, we will not need to introduce additional processes or materials in the fabrication stage, which can reduce the operational cost. Therefore, in this study, we constructed seven types of GBs into the basal plane of 2H MoS<sub>2</sub> nanostructure and determined their catalytic performances to reduce CO<sub>2</sub> to CO by performing density functional theory (DFT) calculations. Since GBs are great sources or sinks for point defects such as vacancies [33], we also investigated the activity of CO<sub>2</sub>RR by introducing single sulfur vacancies (SVs) to the constructed boundaries. Throughout this thesis, we will use 'GB<sub>SV</sub>' and 'SV GBs' interchangeably to refer to GBs incorporated with sulfur vacancies.

Our calculations show that most GB structures obtain better catalytic activities towards CO<sub>2</sub>RR compared to the MoS<sub>2</sub> basal plane. Vacancy-decorated GBs can further reduce the energies for potential-determine steps, indicating the enhancement of catalytic activities. These findings are rationalized by determining the electronic properties of the structures, such as density of states and charge analysis. In addition, to address the selectivity of products, scaling relations between the key intermediates, \*COOH and \*CO, are discussed for each configuration. The results show the favor of CO gas formation on pristine GBs, while further reductions into other products are more commendatory for CO<sub>2</sub>RR on SV GBs.

This thesis will begin with a comprehensive literature review of relevant topics, including (a) CO<sub>2</sub>RR reaction mechanisms, (b) current progress of TMDCs used for CO<sub>2</sub>RR, (c) 2D material design principles for electrocatalysis, and (d) current challenges and future trend of research in the field of 2D materials for CO<sub>2</sub>RR (see Chapter 2 Literature Review). The computational details will then be provided along with calculation methodologies (see Chapter 3 Methodology). The research findings will then be presented, followed by detailed discussions on the rationalization and interpretation of results (see Chapter 3 Methodology and 4 Research Findings and Discussion). This thesis will end with a summary of the study and vision of future work (see Chapter 5 Conclusion).

#### 2. LITERATURE REVIEW

The growing concentration of atmospheric carbon dioxide primarily resulted from human activities such as the consumption of fossil fuels has become one of the biggest environmental and social concerns in recent years. With fossil fuels continuing to be the world's primary energy source (84.3% according to bp 2020 energy report), the increasing usage of non-fossil energy, such as solar and wind, is in high demand [34]. However, the intermittence of renewable energy is one of their drawbacks. As a result, reducing CO<sub>2</sub> efficiently into other valuable raw materials becomes a pressing need. There are six types of CO<sub>2</sub> transformation, which include chemical, photochemical, electrochemical, biological, reforming, and inorganic transformations [1]. Within all these strategies, electrochemical reduction of CO<sub>2</sub> stands out mainly because (1) it can operate under ambient conditions, (2) the product/reaction can be easily adjusted by external parameters such as applied voltages, and (3) the reactions can be driven by renewable energies which generate no extra greenhouse gases [6, 7].

There are different strategies to control the product of electrochemical  $CO_2$  reduction reactions. One strategy is to tune reaction conditions such as pH [35-37], applied potential, temperature [38, 39], and  $CO_2$  pressure [40, 41]. The other strategy is to change the details of chemicals/materials used inside the catalytic cell, which can be achieved via the following routes (among others):

(1) *Varying the electrolyte composition/concentration*. This can suppress the competing hydrogen evolution reaction (HER) by increasing the solubility of CO<sub>2</sub> and changing the local pH [42, 43], stabilize intermediates or cause the surface reconstruction;

- (2) *Catalyst type/structural modification*. Depending on the types of catalytic materials, a wide range of products, from hydrocarbons to oxygenates, can be formed; and
- (3) Modifying the membrane separating the analyte and catholyte [44]. Anion exchange, cation exchange, and bipolar membranes are three common types of membranes. Among these, anion exchange membranes are believed to be favored in CO2 electrolyzers since they can suppress the competing HER reaction by allowing an alkaline environment[45].

The focus of this section will be the choice and tailoring of catalyst materials for CO<sub>2</sub> electrolytic reductions.

Compared to conventional three-dimensional materials, two-dimensional materials are of particular interest due to their large surface area, maximum charge transferability, high electrical conductivity, and mechanical flexibility [46]. MXenes (i.e., transition metal carbides, nitrides, or carbonitrides) [47-51], group-pnictogens (VA) element materials (e.g., black phosphorus (BP), Arsenic (As), Antimony (Sb), and Bismuth (Bi)) [52, 53], TMDCs [23, 29, 30, 54-57], carbon-based materials (e.g., graphene, reduced graphene oxide (rGO), and carbon-nitrides) [58-71], hexagonal boron nitride (h-BN) [72-75], and metal organic frameworks (MOFs) [76-78] are all popular types of 2D material for CO<sub>2</sub>RR, as shown in Figure 2-1. There are various ways to design a catalyst to enhance its catalytic performance, including defect engineering, heterostructure formation, alloying, faceting, and many more. All the methods essentially tune the electronic properties of the material, and therefore affecting its catalytic performance.

This chapter will begin with the reaction mechanism of CO<sub>2</sub>RR to better understand the importance of recognizing reaction steps. Then, current progress on TMDCs used for CO<sub>2</sub>RR

will be discussed. Finally, by introducing the 2D material design principles and challenges of the present status, we present the motivation of our current study,



Figure 2-1. Different types of 2D materials [79].

#### 2.1 Reaction Mechanisms of Electrochemical CO<sub>2</sub>RR

		<b>Electrode Potentials</b>
Reaction	Product	(V vs. SHE) at pH 7
$CO_2 + e^- \rightarrow CO_2^-$	CO <sub>2</sub> <sup>-</sup> anion radical	-1.90
$CO_2+2H^++2e^- \rightarrow HCOOH$	Formic Acid (HCOOH)	-0.61
$CO_2+2H^++2e^- \rightarrow CO+H_2O$	Carbon Monoxide (CO)	-0.53
$CO_2+4H^++4e^- \rightarrow HCHO+H_2O$	Formaldehyde (HCHO)	-0.48
$CO_2+6H^++6e^- \rightarrow CH_3OH+H_2O$	Methanol (CH <sub>3</sub> OH)	-0.38
$CO_2+8H^++8e^- \rightarrow CH_4+2H_2O$	Methane (CH <sub>4</sub> )	-0.24
$2H^++2e^- \rightarrow H_2$	Hydrogen (H <sub>2</sub> )	-0.41

Table 2-1. Main C1 products of CO<sub>2</sub>RR and reactions related to CO<sub>2</sub>RR [80]

 $CO_2RR$ , regardless of the catalyst's dimensionality, involves multiple proton-electron transfers, leading to different types of products. The products are characterized and named by the number of carbon atoms in the molecules. For example, C1 stands for products that include one carbon atom (e.g., CO, CH<sub>4</sub>, and CH<sub>3</sub>OH), and C2 stands for products that include two carbon atoms (e.g., ethanol and ethylene). The reaction mechanism becomes more complex when the number of carbon atoms in the product increases. As shown in Figure 2-2, the number of elementary steps required (~20) to form 1-propanol (C<sub>3</sub>H<sub>8</sub>O), is way higher than that (~6) for methanol. Figure 2-3 schematically shows the proposed reaction pathways from water-dissolved  $CO_2$  to various C1 and C2 products. All products, except formate (HCOO<sup>-</sup>), originate from the reduction of CO, highlighting the importance of CO. If the CO adsorbs to the catalyst material strongly, further reductions to other C1 or C2 products are favorable. While if the adsorption is weak, CO is more likely to leave the material and becomes CO gas. For multi-carbon products, C-C coupling takes place. The boxes highlighted in solid colors in Figure 2-3 are the key products formed, and those highlighted in gradient are the key branching intermediates that promote the formation of a few products. The figure also suggests that early CO dimerization (i.e., C-C coupling occurs before the cleavage of at least one of the C-O bonds) occurs for the formations of ethylene (C<sub>2</sub>H<sub>4</sub>, final product of the red pathway), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH, final product of the blue pathway), and acetaldehyde (CH<sub>3</sub>CHO, one product of the grey pathway) [81]. There are many reaction conditions, such as pH [35], applied potential [39, 82], \*CO coverage/CO partial pressure [39, 83, 84], cation-induced fields [83, 85, 86], and catalyst strain[83], that can affect CO dimerization.

For all reactions, the CO<sub>2</sub> molecule first absorbs an electron and forms CO<sub>2</sub><sup>-</sup> anion radical adsorbed on the material surface. However, this one-electron reduction process is highly energetic and unstable due to the high overpotential (-1.90V vs. standard hydrogen electrode (SHE)). In contrast, proton-assisted electron transfers are more favorable due to their lower redox potentials, ranging from -0.2 to -0.6V vs. SHE, as shown in Table 2-1. Different products may be formed depending on the number of electron-proton pairs that the CO<sub>2</sub> countered with. However, since the products obtain very similar redox potentials, it becomes super challenging to control the selectivity of products. In addition, in aqueous electrolytes, the hydrogen evolution reaction with similar redox potential (-0.41V vs. SHE) competes with CO<sub>2</sub> reduction reactions, which also affects the selectivity of products.



Figure 2-2. Relation between number of carbons in the CO<sub>2</sub>RR product and the steps required to reach the product [87].



Figure 2-3. Pathways for CO<sub>2</sub>RR into C1 and C2 products [81].

### 2.2 TMDCs for CO<sub>2</sub>RR

Transition metal dichalcogenide is a semiconductor of MX<sub>2</sub> type, where M is the transition metal atoms (e.g., Mo, Se, Pt, Ni, etc.) sandwiched between two layers of chalcogen atoms (e.g., S, Se, Te, etc.). The two phases of the structures are shown in Figure 2-4. Their unique electrical, mechanical, and optical properties, which can compensate for graphene (conductor) and h-BN (insulator), and therefore received a lot of attention [21, 22]. Since Asadi et al. found that CO<sub>2</sub> can be reduced to CO at an extremely low overpotential of 54mV on molybdenum disulfide edges, many other studies were conducted to discover TMDCs' potentials for CO<sub>2</sub>RR [23, 29]. The main challenge of this type of material is its low efficiency and selectivity towards CO<sub>2</sub>RR.



Figure 2-4. Top and side views of TMDCs [88].

Abbasi et al. studied the effect of Nb and Ta doping in  $MoS_2$ . The Gibbs free energy diagram for investigated Nb-doped  $MoS_2$  structures (Figure 2-5(A)) is shown in Figure 2-5 (B). NbS<sub>2</sub> required the least energy for CO desorption, while it had the highest energy for COOH adsorption. On the other hand, the energy for CO desorption on  $MoS_2$  showed the highest, while during COOH adsorption, more energy was required compared to all the three other configurations. This trend is schematically presented in Figure 2-5 (C), and it revealed that MoS<sub>2</sub> with the first layer doped with Nb (MoS<sub>2</sub>-Nb-1) could achieve better catalytic performance. In addition, their experimental results showed that Nb doping enhanced the catalytic performances of CO<sub>2</sub>RR, while Ta doping showed the opposite, indicating that the proper choice of the doping element was essential. Thereby, Hong et al. investigated how different doped MoS<sub>2</sub> affects the scaling relations for CO<sub>2</sub>RR [56]. The importance of scaling relationships will be discussed in the following section (2D Materials Design for CO<sub>2</sub>RR). The study showed that CO\* binding was significantly weaker than the binding of COOH\*, CHO\*, and COH\* on the sulfur sites of doped sulfur edges. Their results also suggested that the linear scaling relationship could be broken by changing binding sites for different intermediates (i.e., COOH\*, CHO\*, COH\*, and CO\*), see Figure 2-6 and Figure 2-12.



*Figure 2-5. (A) Different Nb-doped MoS*<sub>2</sub> *structures, (B) Gibbs free energy changes for the reaction steps form CO*<sub>2</sub> *to CO, and (C) the energies required for COOH adsorption and CO desorption [30].* 



*Figure 2-6. Scaling relationships between (left) \*COOH and (right) \*COH and CO for transition-metal doped MoS*<sub>2</sub> *(edges), bare metal 111 surfaces, and bare metal 211 surfaces [56].* 

More recently, Ji et al. systematically studied how basal plane vacancies activated TMDCs towards CO<sub>2</sub>RR and how the density of vacancies affects the scaling results [57]. The study suggested that group V and VI TMDCs suffer from either OH poisoning or low selectivity (i.e., HER selective). In contrast, group X TMDCs did not show either of these behaviors (Figure 2-7 (c)), which led to further investigations. Figure 2-7 shows the scaling relationships of group X TMDCs with various vacancies. The figures demonstrate that when the number of vacancies increases, the binding strength with either COOH, CHO, H, or OH increases, indicating that the density of vacancies can tune the energetics.



Figure 2-7. Binding energies of (a) COOH\* and (b) CHO\* vs. CO\* on group X TMDs with different number of vacancies. (c) Binding energies of H and OH on PtS<sub>2</sub> and PtS<sub>2</sub> with varying percentage of vacancies [57].

Besides doping and vacancy formation, alloying and hybrid-structure formation have also been examined. Xu et al. successfully synthesized a ternary TMDC alloy (MoSeS), which attained a high FE of 45.2% (MoS<sub>2</sub>: 16.6% and MoSe<sub>2</sub>: 30.5%) for CO production at -1.15V vs. RHE [54]. Li et al. grew MoS<sub>2</sub> vertically on N-doped carbon, and this hierarchical hybrid structure exposed a large number of active sites along the edge of MoS<sub>2</sub>, resulted in a low onset potential of about 40 mV, as well as a high CO production rate of 34.31 mA/cm<sup>2</sup> with 92.68 FE at an overpotential of 590 mV [31].

#### 2.3 2D Materials Design for CO<sub>2</sub>RR

As mentioned in the previous section, there are many ways to enhance the catalytic performance by tuning a material, such as doping, adatom, defect engineering, and forming heterostructures. The critical theory behind these is to tune the electronic properties of such materials.

D-band center is a good indicator of surface-adsorbate interactions. Hammer and Nørskov first proposed the theory in 1995 to explain why gold is more inert than other metals [89]. By comparing H<sub>2</sub> dissociation on different metals and studying their electronic structures, they concluded that the degrees of both the filling of the antibonding states upon adsorption and orbital overlap with the adsorbate contribute to the bonding between the adsorbate and adsorbent. Figure 2-8 shows the interaction between the adsorbate (s and d states) and the transition-metal adsorbent. The coupling of s band and metal results in a broadening and shift of the adsorbate state. However, since the band is broad and all transition metals have a half-filed s-band, the sstates will not vary much among the transition metals [90, 91]. Indeed, the formation of antibonding and bonding states in the adsorbate, when coupled to metal d states, play a much more critical role in determining their bonding strength. When there is less filling of the antibonding state, the interaction between the metal and adsorbate will be more stabilized (i.e., stronger bonding). D-band center, a quantity that can be easily determined experimentally or computationally, is a good indicator for filling an antibonding state. When the d-band center is closer to the Fermi level, the antibonding state will be less filled, and therefore stronger bonding between the adsorbate and metal. Figure 2-9 (B) and (C) show the density of state (DOS) diagrams for CO adsorbed on Ag and WSe<sub>2</sub> nanoflakes (NFs). Since WSe<sub>2</sub> obtains a d-band center closer to the Fermi level than Ag, stronger interactions between the metal and CO should be observed for WSe<sub>2</sub>. This stronger interaction corresponds to the uprising of energy during the last step (i.e., CO desorption step) in Figure 2-9 (A). For a non-metal surface/atom to which the adsorbate bonds, the p-band center instead of the d-band center is used because the adsorbate and the non-metal form sigma-pi ( $\sigma$ - $\pi$ ) bonding state instead of sigma-d ( $\sigma$ -d) bonding state.



Figure 2-8. D-band model illustrating bond formation at a transition-metal surface [91].



Figure 2-9.(A) Free energy diagrams for CO<sub>2</sub> reduction to CO on different surfaces. Partial density of states of (B) the surface Ag55 atom and (C) edge W atom of the WSe<sub>2</sub> nanoflakes [23].

Charge characteristics, such as charge transfers and charge densities, are some other factors that can affect adsorptions. For example, in ternary TMDC alloy MoSeS, there is an increase in density of states near the conduction band edge compared to MoS<sub>2</sub> and MoSe<sub>2</sub> (see Figure 2-10 (A), (D), and (G)), which leads to a faster charge transfer, and therefore more conductive compared to the other two. The charges around each structure (Figure 2-10 (B), (E), and (H)) illustrated that the charges are off-centered around Mo and become closer to S in the case of MoSeS, while charges are localized in the center of Mo for the cases of MoS<sub>2</sub> and

MoSe<sub>2</sub>. This off-centered charge phenomenon is created by the structural deformation caused by Mo-S and Mo-Se bond length mismatch. It can stabilize the COOH adsorption and facilitate CO desorption (i.e., overall lower energetics) [54].



Figure 2-10. ensity of states diagrams, cross-sectional views of charge density isosurfaces, and crystal structures for (A)(B)(C) MoSeS, (D)(E)(F) MoS<sub>2</sub>, and (G)(H)(I) MoSe<sub>2</sub> [54].

Linear scaling trends between intermediate poses a significant limitation to the catalytic efficiency of CO<sub>2</sub>RR. Figure 2-11 illustrates how the limiting potentials correspond to the scaling relationships between CHO and CO binding energies on transition-metal 111 and 222 surfaces, as well as how different transition-metal doped MoS<sub>2</sub> obtains different limiting potentials (i.e., broken linear scaling relationship). The rationale behind this broken linear scaling is that the binding configurations of intermediates on the material change when varying doping elements. For example, on Ni-doped edges of MoS<sub>2</sub>, CHO\* tends to bind to the Ni atoms (metallic site), while CO\* bonds with the sulfur atom (covalent site), as shown in Figure 2-12.



Figure 2-11. Limiting potential of the \*CO to \*CHO formation step [56].



Figure 2-12. Binding configurations of CO\* and CHO\* on the edge of Ni-doped MoS<sub>2</sub> [56].

#### 2.4 Challenges and Research Needs of 2D Materials for CO<sub>2</sub>RR

There has been rapid and tremendous progress in 2D materials for catalyzing  $CO_2RR$ , whereas some challenges still exist experimentally and theoretically.

Since the ideal catalyst should have high efficiency, faradic efficiency, selectivity, stability, and small overpotential, finding a material containing all these criteria remains difficult. Surface modifications such as doping, defect, curvature, and strain engineering can improve the catalytic performance of 2D materials, but precisely control the modifications is still challenging for large-scale productions. The trend would be to look for imperfections that naturally exist after production as active sites (e.g., GB defects) or modifications that persist high tolerance during production (e.g., defects that do not depend hugely on the defect concentration).

Computationally, most studies only focus on the catalyst material itself, causing other operating parameters such as electrolyte acidity, pressure, and details about the electrolytic cells to remain left out. Therefore, combining experiments with computational work will provide a more comprehensive view of the performance of a chosen system.

Since linear scaling relationships between intermediates can significantly hinder the material's performance, more study should be done, theoretically, to break this linear scaling relation. Some structural modifications have been shown to break this scaling. However, the rationale behind this remains unanswered. More understandings of the structure-property relationships are essential to bringing the current material research status to the next level. Moreover, the reaction mechanisms remain ambiguous for many systems, probably because most studies are still theoretical without in-situ observations complimented. Again, experiment and computational work can complement each other.

Last but not least, some types of materials, such as h-BN, MXene, and group VA 2D catalysts, are still in their novice stage; more studies on their activation strategies should be done.

#### 3. METHODOLOGY

#### **3.1 Model Construction**

In this study, a series of GBs of 2H MoS<sub>2</sub> monolayers are constructed to investigate the catalytic performances towards CO<sub>2</sub>RR. Figure 3-1 (a) shows an optimized geometrical configuration of MoS<sub>2</sub> monolayer consisting of  $1 \times 1$  unit cells. Due to the D3h symmetry of 2H MoS<sub>2</sub>, there exist two edge configurations, namely zig-zag- $\alpha$  (ZZ- $\alpha$ ) and zig-zag- $\beta$  (ZZ- $\beta$ ) edge, for a GB along the zigzag (ZZ) direction (See Figure 3-1 (a)). On the other hand, GBs along the armchair (AC) direction have the same edge configuration, which can be unambiguously indicated as AC edge. Different edge configurations and local bonding environments lead to several types of GBs. Figure 3-1 (b)-(h) shows the configurations of the stable GB structures after geometry relaxation. We further describe these GBs by their ring compositions in the boundary region. For example, 5/7 GB is composed of 5- and 7-element rings, while 4/4 GB is composed of 4-element rings.

#### **3.2 Computational Details**

All the calculations were performed by employing spin-polarized density functional theory (DFT) within a general gradient approximation parametrized by Perdew, Burke, and Ernzerhof (GGA-PBE), as implemented in the Vienna ab initio simulation package (VASP) [92-96]. The electron-ion potential was described by the projected augmented wave method, and a kinetic energy cut-off of 520 eV was used for the plane wave expansion. All structures were relaxed until the atomic forces were less than 0.01 eV/Å, and total energies were converged to  $10^{-5}$  eV. Meanwhile, all GB structures are constructed using nanoribbon models to avoid any

dissatisfaction caused by asymmetry and to evaluate GBs' formation energy accurately. Benchmark calculations have been performed to ensure that the separation between the nanoribbon edges is sufficiently large (greater than 20 Å) to avoid any artificial effect arising from edge-edge or edge-boundary interactions (See Figure S1 in Appendices). The vacuum spaces in all supercells were larger than 15 Å above the MoS<sub>2</sub> plane to avoid any artificial interaction. DFT-D2 method of Grimme was used to address any Van der Waals (vdW) interactions resulting from dynamical correlations between fluctuating polarizations of molecules [97].



Figure 3-1. (a) The top and side views of pristine MoS<sub>2</sub> with AC edges and ZZ edges, and the top views of the relaxed configurations of (b) 5/7a, (c) 5/7b, (d) 4/8a, (e) 4/8b, (f) 8/8a, (g) 8/8b, and (h)4/4 GBs, where Mo atoms are shown in purple and S atoms are shown in yellow.

#### **3.3 Calculation Methodologies**

#### 3.3.1 Formation Energies of MoS<sub>2</sub> GBs

Before determining the adsorption energy of different GBs, formation energies are calculated to ensure the ease of forming of GBs. The presence of edges needs to be taken into consideration while doing such calculation, and the formation energy,  $E_f$ , can be determined from the total energy,  $E_T$ , of the structure:

$$E_T = N_{M_0} \mu_{M_0} + N_S \mu_S + L \left( \left( \sigma_{ZZ, \alpha} + \sigma_{ZZ, \beta} + \sigma_{AC} \right) + E_f \right)$$
(1)

where  $N_{Mo}$  and  $N_S$  are the numbers of Mo and S atoms in the structure, respectively, *L* is the GB length,  $\sigma_{ZZ,\alpha}$ ,  $\sigma_{ZZ,\beta}$ , and  $\sigma_{AC}$  are the formation energies of ZZ- $\alpha$ , ZZ- $\beta$ , and AC edges per unit length, respectively, and  $\mu_{Mo}$  and  $\mu_S$  are the chemical potentials of Mo and S, respectively. The chemical potentials depend heavily on the experimental conditions. In this research, the upper and lower limits of  $\mu_S$  are defined by the chemical potentials of 1/8 octathiocane (S8) and body-centered cubic Mo, respectively, thus ranging from -4.14 eV to -5.40 eV. To maintain thermodynamic equilibrium, the allowable range of  $\mu_{Mo}$  and  $\mu_S$  are constraint by the following condition:

$$\mu_{\rm MoS2} = \mu_{Mo} + 2\mu_{\rm S} \tag{2}$$

 $\sigma_{AC}$  can be calculated by the energy of pristine MoS<sub>2</sub> with AC edges (Figure 3-1 (a)), E<sub>AC</sub>:

$$\sigma_{\rm AC} = (E_{\rm AC} - N_{M_0} \mu_{M_0} - N_{\rm S} \mu_{\rm S})/2L \tag{3}$$

 $\sigma_{ZZ,\alpha}$  and  $\sigma_{ZZ,\beta}$  have the relation of:

$$\sigma_{ZZ,\alpha} + \sigma_{ZZ,\beta} = (E_{ZZ} - N_{Mo} \mu_{Mo} - N_{S} \mu_{S})/L$$
(4)

where  $E_{ZZ}$  is the energy of pristine MoS<sub>2</sub> with ZZ edges (Figure 3-1(a)).

 $\sigma_{ZZ,\beta}$  can be determined by constructing a series of triangular quantum dots (Figure 3-2) and plot the relationship between f(n) and the size of the quantum dot, n [98]:

$$f(n) = E_{tri}(n) - n(n+1)/2 * \mu_{MoS2} = (2\mu_S + 3\sigma_{zz,\beta})n + 3E_{cor} + 2\mu_S$$
(5)

where  $E_{tri}(n)$  is the energy of the triangular quantum dot, and  $E_{cor}$  is the energy of the three corners of the quantum dot.  $\sigma_{zz, \beta}$  can be determined by the slop of the f(n) vs. n plot (i.e.,  $2\mu_{s}+3\sigma_{zz, \beta}$ ). The plot is presented in Figure S2 in Appendices.

The formation energy can finally be calculated using Eq.1 with  $\sigma_{ZZ, \alpha}$ ,  $\sigma_{ZZ, \beta}$ , and  $\sigma_{AC}$  being the solutions of Eq. 5, 4, and 3, respectively.



Figure 3-2. Quantum dot constructions for (a) n=5 and (b) n=11, where Mo atoms are shown in purple and S atoms are shown in yellow.

#### 3.3.2 Formation Energy of Vacancies

The formation energy of single vacancy, E<sub>f,SV</sub> is calculated by:

$$E_{f,SV} = E_{SV} - E - \mu_S \tag{11}$$
where  $E_{SV}$  and E are the energy of MoS<sub>2</sub> with and without S vacancy, respectively, and  $\mu_S$  is the chemical potential of elemental sulfur taken as the chemical potentials of 1/8 S8 in this case.

### 3.3.3 Gibbs Free Energy

A three-step reaction mechanism via a two-electron pathway is considered in this study to calculate the free energy diagrams:

Step 1: 
$$CO2 + H+(aq) + e^{-} + * \rightarrow *COOH$$
 (12)

Step 2: 
$$*COOH + H+(aq) + e \rightarrow *CO+H2O$$
 (13)

Step 3: 
$$*CO \rightarrow CO + *$$
 (14)

where \* indicates a free step site. The first two steps are potential dependent, while the last step is a desorption process that proceeds without electrons.

The Gibbs free energy change,  $\Delta G$ , can be calculated as:

$$\Delta G = \Delta E_{ads} + \Delta E_{corr} \tag{15}$$

where  $\Delta E_{ads}$  is the adsorption energy of intermediates (i.e., \*COOH and \*CO) and  $\Delta E_{corr}$  is the change of correction energy. Free energy corrections are calculated by adding the zero-point energies (ZPE), entropies (S), and heat capacities (C<sub>p</sub>), calculated with the harmonic oscillator approximation where all degrees of freedom were treated as harmonic vibrations:

$$E_{corr} = ZPE + \int C_p dT - TS$$
(16)

in which the temperature, T, is taken as room temperature (298.15K). The energy corrections for non-adsorbed species, namely CO<sub>2</sub>, CO, H<sub>2</sub>, and H<sub>2</sub>O, are listed in

Table S1 in Appendices. All gaseous species (i.e., CO<sub>2</sub>, CO, and H<sub>2</sub>) are assumed to have a fugacity of 101325 Pa. The free energy of liquid water is calculated as an ideal gas and adjusted to a fugacity of 3534 Pa, which is the vapor pressure of water at room temperature. For adsorbed species (i.e., \*COOH and \*CO), the correction energies differ from case to case, and they are listed in Table S2 in Appendices. CO\* is assumed to be adsorbed species even when lightly or not adsorbed onto the surfaces.

## 3.3.4 Electronic Properties

Electronic properties, such as band center, electron transfer, and charge density, are critical in the field of electrocatalysis, and it has been briefly discussed in section 2.3. This part presents how we calculated some of these properties.

Since the p-band center is the center value of the p-band energy state, it can be calculated by:

$$\varepsilon_p = \frac{\int_{-\infty}^{\infty} \varepsilon \rho_p(\varepsilon) d\varepsilon}{\int_{-\infty}^{\infty} \rho_p(\varepsilon) d\varepsilon}$$
(17)

where  $\epsilon$  is the energy level (eigenvalue), and  $\rho_p$  is the density of p electronic state at  $\epsilon$ .

Charge density difference isosurfaces ( $\Delta \rho$ ) are calculated using:

$$\Delta \rho = \rho_{\text{Total}} - \rho_{\text{MoS2}} - \rho_{\text{ads}} \tag{18}$$

where  $\rho_{Total}$  and  $\rho_{MoS2}$  are the charge densities of the systems with and without adsorbates, and  $\rho_{ads}$  is the charge density of the adsorbate (i.e.,  $\rho_{COOH}$  and  $\rho_{CO}$  for COOH and CO adsorption, respectively).

#### 4. RESEARCH FINDINGS AND DISCUSSION

#### 4.1 Formation Energies of GBs

The formation energy for different GBs at varying  $\mu_s$  is provided in Figure 4-1. The GBs of nanoribbons with zig-zag- $\beta$  edges (i.e., 4|4, 4|8b, and 8|8b) generally have negative formation energies, meaning their ease of forming. In contrast, those with armchair edges (i.e., 5|7a, 5|7b, and 4|8a) have positive formation energy, indicating that energy would be needed for the GBs to form. However, the energies are small (less than 1 eV) and achievable. However, the gain boundary with the zig-zag- $\alpha$  edge (i.e., 8|8a) obtains very high formation energy – from 3.68 to 1.21 eV for Mo-rich and S-rich cases, respectively. The high formation energy of the 8|8a GB indicates its instability and difficulty forming and is therefore not included in further discussions in this study.

The positive, zero, and negative slopes for different GB systems in Figure 4-1 result from the deficiency or excess of S (or Mo). When there is an excess of sulfur atoms (i.e., N<sub>S</sub>: N<sub>Mo</sub> > 2:1), the formation energy decreases with increasing  $\mu_S$ ; when there is an excess of molybdenum atoms (i.e., N<sub>S</sub>: N<sub>Mo</sub> < 2:1), the formation energy increases with increasing  $\mu_S$ . The formation energy has no dependency with  $\mu_S$  when there is neither access nor deficiency in sulfur (i.e., N<sub>S</sub>: N<sub>Mo</sub> = 2:1).



Figure 4-1. Formation energies of the GBs as functions of the chemical potential of S,  $\mu_s$ .

## 4.2 Gibbs Free Energy



Figure 4-2. (a) Energetics of the CO<sub>2</sub>RR process on different MoS<sub>2</sub> GBs (b) Energetics of the CO<sub>2</sub>RR process on different MoS<sub>2</sub> SV GBs.

The free energies for the reactions at different GBs of  $MoS_2$  are presented in Figure 4-2(a), with numeric details presented in Table S3 to Table S5 in Appendices. It can be seen from the figure that the Gibbs free energy of all the adsorption sites in defect regions are smaller than that of the perfect  $MoS_2$  basal plane (2.30 eV), except for 4|4 which has a free energy of 2.36 eV. This lowering of energy indicates that GBs can indeed break the inertia of the basal plane and enhance the interaction between the COOH molecule and the adsorption site. Step 1 appears to be the energy determine steps for all cases. The stronger interaction between carbon and sulfur in step 1, the lower energy is needed for the COOH molecule to be adsorbed onto the GB. This interaction can be confirmed by determining the C-S bond length, as shown in Figure 4-3 (a). Figure 4-3 (b) shows the side view of COOH adsorption on the 4|8b GB as a representative. Most GB structures are very inert in terms of CO adsorption (i.e., weak bonding with CO), except for 5/7b and 4/8a GBs shown in Figure S3 (d) and (e), and this explains the downward behavior of step three (i.e., CO desorption). However, the uprisings of energy for 5|7b and 48 a GBs in step 2 are abnormal and contradict bonding prediction (i.e., a stronger bond leads to lower adsorption energy). This deviation is probably due to the vast system used where the physisorption caused by Van der Waals forces surplus the chemisorption [99]. It can also be caused by the elongated CO bond, as shown in Figure 4-4.



Figure 4-3. (a) Relationship between  $\Delta E$  and C-S bond length of COOH adsorption on clean GBs. (b) Side view of COOH adsorption on 4/8b GB, with color label below the figure<sup>1</sup>.



Figure 4-4. The side view of CO adsorptions on (a)4/8a, (b)5/7b, and (c)4/4 GBs, with CO lengths labeled.

Although GB defects visibly enhance catalytic CO<sub>2</sub> reduction, the free energy is not much superior to some systems studied by others. In addition, because point defects like vacancies are easy to form in GBs, GBs with single vacancies are constructed to understand the catalytic behavior better.

<sup>&</sup>lt;sup>1</sup> This color label will be used consistently throughout the thesis

We started by looking at the formation energy of vacancies on GBs. All GBs show similar or lower sulfur vacancy formation than the basal plane (2.86 eV), with 8|8a being the lowest (0.23 eV) and 4|8a the highest (2.95 eV). The low formation energy of a single vacancy on 8|8a GB also confirms the high energy of the GB. The numeric details are presented in Table S6 in Appendices. The free energies for the three reactions at different GBs with one S vacancy are presented in Figure 4-2 (b). All GBs show better catalytic performance when an S vacancy is appended. This overall lower energy can be rationalized by the change of binding sites of intermediates.

Figure 4-5 shows that the carbon atom is bonded with molybdenum atoms instead of sulfur when the GB is defective. 4|4 GB is used as a representative here; adsorption configurations for other structures are provided in Figure S3 to Figure S6 in the Appendices. Step 1 appears to be the energy determine steps for all cases, without taking step 3 into consideration. The Gibbs free energies of all the adsorption sites in defect regions are smaller than the perfect MoS<sub>2</sub> basal plane (1.11 eV) except for 5|7a, which has a free energy of 1.23 eV. The competing HER energetics are provided in Figure S11. The competing HER reaction remains to be problematic in our investigated systems, which requires further attentions.



*Figure 4-5. Top view of COOH (a and c) and CO (b and d) adsorption on the pristine (a and b) and defective (c and d) 4/4 GBs.* 

#### **4.3 Scaling Relations**

Many efforts have been made to break the scaling relationship between  $CO_2$  reduction intermediates because the linear scaling limits the catalytic efficiency of transition-metal catalysts. This study determined the adsorption energy scaling relationship between COOH\* and  $CO^*$ , as shown in Figure 4-6.

The \*CO binding energy can describe the capability of GBs to protonate \*CO further. When  $E_b$ (\*CO) is greater than -0.5 eV, CO gas is more likely to form, while when the binding energy is smaller than -0.5 eV, CO is more likely to be further protonated into other products such as \*CHO. It can be seen clearly from Figure 4-6 that pristine GBs promote the formation of CO gas. In contrast, GBs decorated with vacancies promote CO\* bonding to the catalyst surface stably, which is a prerequisite for further reducing \*CO. This also explains why Gibbs free energy downhills in Step 3 in Figure 4-2 (a), but rising in energy are observed in Figure 4-2 (b). Linear scaling relationships can be observed for single-vacancy GB systems. 8|8b and 4|8b GB<sub>SV</sub> show apparent deviation from the linear line, mainly due to the difference of binding sites for the CO<sub>2</sub> reduction intermediates (i.e., COOH and CO). For example, COOH binds with 3 Mo atoms in 8|8b GB<sub>SV</sub>, but CO binds with only 1 Mo atom in the same catalytic structure, as shown in Figure 4-6. Another example would be plain 4|8b GB<sub>SV</sub> – COOH adsorbed onto one sulfur atom while CO is bonded with two sulfur atoms, as shown in Figure 4-6. In contrast, a linear scaling relationship cannot be observed for pristine GB cases since CO is physisorbed onto the GBs for most systems. In addition, the dearth of chemisorbed CO configurations hinders further investigations on the scaling relationship of pristine GBs.



Figure 4-6. Binding energy relationships between  $E_b(COOH)$  and  $E_b(CO)$  for different GBs with and without vacancies. The dotted line approximates the scaling relation of SV GBs. The grey area represents CO physisorption, and the blue area represents CO chemisorption. Magnified top view of COOH and CO adsorptions on 8/8b and 4/8b SV GBs are shown on the left and right side of the figure, respectively.

# **4.4 Electronic Properties**

To further understand the rationale of adsorption energy change of the reactions. The electronic properties of the structures are investigated.

Energy analyses by Huang et al. revealed that the closer an electronic state is to the Fermi energy,  $E_F$ , the greater its contribution to bonding [100]. Therefore, the density of states (DOS) calculation is performed for various cases. The change in p-band centers ( $\epsilon_p$ ) can explain difference in  $E_{ads,COOH}$  in clean GBs. As shown in Figure 4-7, the adsorption energy becomes lower (i.e., bonding is stronger) as the p-band center approaches Fermi level ( $E_F=0$ ). This also illustrates that the adsorption energy can be adjusted by tuning the p-band center. Figure 4-8 (a) and (b) provide the DOS plots for adsorptions on pristine and 5|7b GB, respectively. COOH adsorption on pristine MoS<sub>2</sub> surface shows sulfur 3p bonding state hybrid with carbon 2p state at around -11 eV. In comparison, the hybridization for 5|7b GB happens at about -8 eV, indicating stronger bonding at 5|7b GB, in agreement with the p-band center analysis.



Figure 4-7. Relationship between p-band center and COOH adsorption energy on pristine GBs.



Figure 4-8. DOS plots for (a) pristine MoS2 and (b) 5/7b GB (top panel) before adsorption, (middle panel) after COOH adsorption, and (bottom panel) after CO adsorption.

However, d-band or p-band center theories cannot be applied to other cases due to orbitals from more than one atom contributing to the bonding. In those cases, charge transfer, another deciding descriptor for  $CO_2RR$ , is determined using Bader charge analysis to understand the trends better. When there are more charges transferred from the catalyst to adsorbance, lower adsorption energies are generally absorbed. This explains why a distinct \*COOH binding trend can be observed for systems with and without vacancies in the scaling diagram (Figure 4-6). When a vacancy is comprehended, more excess electrons can be found around COOH and CO. Therefore, stronger \*COOH and \*CO binding can be generally observed in GB<sub>SV</sub> systems. Figure 4-9 provides the number of charges around adsorbance (i.e., COOH and CO) after adsorption concerning the corresponding adjusted adsorption energies, where \* indicates that the respective deformation energies are excluded for more realistic observations. Though a perfectly fitted strict line cannot be observed due to intrinsic properties of GBs, the trend provides a general picture of how charge transfer affects adsorption. CO physisorption is excluded in the figure due to the minuscule number of electrons transferred (i.e., weak Van der Waals forces dominants), which affects the accuracy of observations. The numeric details are provided in Table S8.



Figure 4-9. Number of excess charges on (a) COOH with and without single S vacancies on different GBs, and (b) CO for chemisorption cases, with respect to adsorption energies. Blue and pink shadows highlight the GB and vacancy added GB systems, respectively.

Ligancy, or coordination number, is another discernible factor that manifests the trend of charge transfers. This quantity describes the number of atoms that the adsorbance is adsorbed onto. This research investigated how the carbon coordination number for CO adsorptions on SV GBs affected the binding energies, as listed in Table 4-1. It can be observed that the binding energy decreases with increasing ligancy. However, 8|8b is an unconventional case where the coordination number is minimal while obtaining the lowest binding energy. This peculiarity is probably due to the substantial structural deformation caused to the GB structure after CO adsorption, as shown in Figure 3-1 (g) and Figure S6 (f).

GB	CO Binding Energy (eV)	Coordination Number (Carbon)
4 8b	-0.920	2
5 7b	-1.026	4
5 7a	-1.140	4
basal	-1.154	4
4 8a	-1.271	4
4 4	-1.332	5
8 8b	-2.109	2

 Table 4-1. Carbon ligancy numbers for CO adsorptions on different GBs (with vacancy) with respect to the CO binding energies

To illustrate how adsorbates interact with the GBs and determine bonding, we also spectated the charge density isosurfaces for all configurations, which are provided in Figure S7 to Figure S10 in Appendices. The yellow region represents the negative charge density difference of -0.005 e Bohr<sup>-1</sup>, and the cyan region represents the positive charge density difference of +0.005 e Bohr<sup>-1</sup>. Figure 4-10 (a) and (b) show interactions between CO and 5|7b and 4|8a GBs, respectively, as representatives. Both isosurfaces indicate carbon bonding with both Mo and S. On the 5|7b GB, the carbon atom mainly interacts with the sulfur atom observed by the large charge density around sulfur. On 4|8a GB, the carbon atom also strongly interacts with sulfur, but its interaction with molybdenum is more robust than that on 5|7a GB. The DOS plot (Figure 4-11) of CO adsorption on the two GBs confirms the finding. The 4d bonding between Mo and C is almost negligible on 5|7b GB, and 3p bonding contributes markedly to

both configurations. The bonding of 4|8a GB with CO happens at a higher energy level (~-7eV), indicating a stronger bond, which is confirmed by the free energy diagram (Figure 4-2 (a)).



Figure 4-10. Top and side views of charge distributions for CO adsorptions on (a) 5/7b and (b)4/8a GBs. The yellow region represents the negative charge density difference of -0.005 e Bohr<sup>-1</sup>, and the cyan region represents the positive charge density difference of +0.005 e Bohr<sup>-1</sup>.



Figure 4-11. DOS plots for 4/8a GB (top panel) and 5/7b GB (bottom panel) after CO adsorption.

#### 5. CONCLUSION

#### 5.1 Summary of Research

This study used first-principal calculations to construct and analyze a series of  $2H MoS_2$  nanoribbon with GBs with and without single sulfur vacancies.

Formation energies of each configuration were calculated in order to determine their ease of forming. 8/8a GB was eliminated for further analysis due to its difficulty of forming.

Except for 4|4, all GBs show enhanced catalytic performances, mainly due to reduced Gibbs free energy during reductions. The free energies were further reduced when a sulfur vacancy was added because carbon bonded through molybdenum instead of sulfur. Remarkably, 4|4 GB<sub>SV</sub> showed best catalytic performance among all, while it obtained the highest Gibbs free energy when there was no vacancy.

The linear scaling relationship was broken due to the change of adsorption sites during reactions. Pristine GBs promote the formation of CO gas. In contrast, GBs decorated with vacancies promote CO\* bonding to the catalyst surface stably, which is a prerequisite for further reducing \*CO.

For COOH adsorptions on clean GBs, the change in adsorption energy can be rationalized by changing of sulfur p-band center and bond length. In the cases where the Fermiabundance model fails, charge transfers from the substrate to adsorbates were investigated, and a general trend was observed (i.e., more charge transferred indicating stronger bonding). Ligancy explains trends for CO adsorption on SV GBs. Electronic density of state diagrams was provided to supporting findings.

### **5.2 Recommendations for Further Research**

GBs have shown visible enhancement to CO<sub>2</sub>RR compared to basal planes. However, challenges still exist upon further investigations or improvements. Firstly, the competing hydrogen evolution reaction remains the problem of the explored GB systems, which hugely affects the selectivity and catalytic efficiency. Secondly, only seven types of GB structures are investigated in this research due to computational limitations – a more systematic study encompassing more types of GBs, shifts, and twists is needed for a more profound understanding of this subject. Last but not least, the research on CO<sub>2</sub>RR on 2D materials remains primarily theoretical. Collaboration with laboratory work is needed to test the results from DFT calculations, as well as to examine the experimental feasibilities.

To future our research, we plan to investigate different types of GBs and their modification methods, such as doping and alloying, more systematically. Meanwhile, experimental validation will also be a critical component, which may be achieved through collaborations with experimental groups.

## 5.3 Significance of the Study

In summary, despite the limitations mentioned above, our study shows that defect engineering via GB and vacancy can activate carbon dioxide reduction on MoS<sub>2</sub> monolayer, providing valuable insights towards designing a new class of high-performance CO<sub>2</sub>RR electrocatalysts.

## **APPENDICES**



Figure S1. Energies of 5/7b structures with different edge separation distances (i.e., vacuum distances between adjacent edges).



Figure S2. Linear fitting of f with respect to n.

Molecule	ZPE (eV)	$\int C_p dT(eV)$	-TS (eV)	ΔE <sub>corr</sub> (eV)	
CO <sub>2</sub>	0.31	0.10	-0.66	-0.26	
СО	0.13	0.09	-0.61	-0.39	
$H_2$	0.27	0.09	-0.40	-0.04	
H2O	0.57	0.10	-0.67	0.00	

Table S1. Free energy corrections ( $\Delta E_{corr}$ ) for non-adsorbed species

Table S2. Free energy corrections (AEcorr) for adsorbed species on different GBs

	GB	$\Delta E_{corr, COOH^*}(eV)$	$\Delta E_{corr, co^*} (eV)$
	4 4	0.55	0.04
	5 7a	0.53	0.05
	4 8b	0.56	0.06
Pristine	5 7b	0.53	0.12
	basal	0.52	0.01
	4 8a	0.54	0.14
	8 8b	0.51	0.01
	4 4	0.53	0.13
	5 7a	0.60	0.14
	4 8b	0.58	0.14
SV	5 7b	0.58	0.18
	basal	0.60	0.15
	4 8a	0.59	0.14
	8 8b	0.58	0.16



Figure S3. The COOH adsorption configurations for (a) basal, (b) 5/7a, (c)5/7b, (d)4/8a, (e) 4/8b, and (f) 8/8b GBs.



Figure S4. The CO adsorption configurations for (a) basal, (b) 5/7a, (c)5/7b, (d)4/8a, (e) 4/8b, and (f) 8/8b GBs.



Figure S5. The COOH adsorption configurations for (a) basal, (b) 5/7a, (c)5/7b, (d)4/8a, (e) 4/8b, and (f) 8/8b  $GB_{SV}$ .



Figure S6. The CO adsorption configurations for (a) basal, (b) 5/7a, (c)5/7b, (d)4/8a, (e) 4/8b, and (f) 8/8b GB<sub>SV</sub>.

	GB	$\Delta E_{ads}$ (eV)	ΔE <sub>corr</sub> (eV)	ΔG (eV)
	4 4	1.54	0.83	2.37
	5 7a	0.64	0.81	1.44
	4 8b	0.28	0.84	1.12
Pristine	5 7b	0.62	0.81	1.43
	basal	1.48	0.80	2.29
	4 8a	0.65	0.82	1.47
	8 8b	0.97	0.79	1.75
	4 4	-0.88	0.81	-0.07
	5 7a	0.41	0.88	1.29
	4 8b	-0.40	0.86	0.46
SV	5 7b	0.07	0.86	0.92
	basal	0.29	0.88	1.17
	4 8a	-0.44	0.87	0.43
	8 8b	-0.25	0.86	0.61

Table S3. Free energy change of each configuration for step 1

	GB	$\Delta E_{ads}$ (eV)	ΔE <sub>corr</sub> (eV)	ΔG (eV)
	4 4	-0.67	-0.48	-1.15
	5 7a	0.04	-0.46	-0.41
	4 8b	0.71	-0.48	0.23
Pristine	5 7b	1.81	-0.39	1.41
	basal	-0.84	-0.49	-1.33
	4 8a	1.28	-0.38	0.89
	8 8b	-0.06	-0.47	-0.54
	4 4	0.27	-0.38	-0.11
	5 7a	-0.83	-0.43	-1.26
	4 8b	0.20	-0.42	-0.22
SV	5 7b	-0.37	-0.38	-0.75
	basal	-0.72	-0.43	-1.15
	4 8a	-0.11	-0.43	-0.54
	8 8b	-1.13	-0.40	-1.53

Table S4. Free energy change of each configuration for step 2

	GB	$\Delta E_{ads}$ (eV)	ΔE <sub>corr</sub> (eV)	$\Delta G (eV)$
	4 4	-0.15	-0.43	-0.58
	5 7a	0.05	-0.44	-0.39
	4 8b	-0.27	-0.44	-0.71
Pristine	5 7b	-1.70	-0.51	-2.21
	basal	0.08	-0.40	-0.32
	4 8a	-1.20	-0.53	-1.73
	8 8b	-0.18	-0.40	-0.58
	4 4	1.33	-0.52	0.82
	5 7a	1.14	-0.53	0.61
	4 8b	0.92	-0.53	0.39
SV	5 7b	1.03	-0.56	0.46
	basal	1.15	-0.54	0.62
	4 8a	1.27	-0.53	0.74
	8 8b	2.11	-0.54	1.56

Table S5. Free energy change of each configuration for step 3

GB	E <sub>f,SV</sub> (eV)
4 4	2.87
5 7a	2.32
4 8b	1.94
5 7b	2.30
basal	2.86
4 8a	2.95
8 8b	2.41
8 8a	0.23

Table S6. Vacancy formation energies for different GB structures

Table S7. P-band center for COOH adsorption on pristine GBs

GB	P-Band Center (eV)
basal	-5.63
4 4	-5.65
4 8b	-4.24
5 7a	-4.48
5 7b	-4.50
8 8b	-4.76
<b>4</b>  8a	-4.65

		COOH Adsorption				CO Adsorption			
		ec	eo	eo	ен	eTotal	ec	eo	eTotal
	basal	1.46	-0.97	-0.67	0.16	-0.01	0.90	-0.92	-0.02
	4 4	1.43	-0.95	-0.89	0.41	0.00	1.00	-1.02	-0.01
	8 8b	1.42	-0.93	-0.78	0.32	0.03	0.81	-0.85	-0.04
Pristine	4 8b	1.37	-0.96	-0.87	0.27	-0.19	0.70	-0.77	-0.07
	5 7a	1.15	-0.84	-0.73	0.18	-0.24	0.91	-1.01	-0.10
	5 7b	1.41	-1.00	-0.79	0.15	-0.24	0.44	-0.53	-0.10
	4 8a	0.91	-0.62	-0.61	0.12	-0.18	0.50	-0.69	-0.19
	4 4	0.04	-0.71	-0.75	0.37	-1.05	0.17	-0.74	-0.58
	5 7a	0.35	-0.96	-0.77	0.43	-0.94	-0.23	-0.67	-0.90
	4 8b	0.52	-0.92	-0.74	0.42	-0.72	0.38	-0.77	-0.40
SV	5 7b	0.19	-0.97	-0.60	0.35	-1.04	-0.38	-0.71	-1.09
	basal	0.32	-0.90	-0.71	0.40	-0.89	-0.05	-0.73	-0.78
	4 8a	0.24	-0.81	-0.77	0.40	-0.93	-0.15	-0.68	-0.83
	8 8b	-0.08	-0.52	-0.91	0.48	-1.04	0.16	-0.86	-0.70

Table S8. Charges around absorbates after adsorptions



Figure S7. Charge distribution for COOH adsorptions on (a) basal, (b) 4/4, (c) 5/7a, (d)5/7b, (e)4/8a, (f) 4/8b, and (g) 8/8b GBs.



Figure S8. Charge distribution for CO adsorptions on (a) basal, (b) 4/4, (c) 5/7a, (d) 4/8b, and (e) 8/8b GBs.



Figure S9. Charge distribution for COOH adsorptions on (a) basal, (b) 4/4, (c) 5/7a, (d)5/7b, (e)4/8a, (f) 4/8b, and (g) 8/8b GB<sub>SV</sub>.



Figure S10. Charge distribution for CO adsorptions on (a) basal, (b) 4/4, (c) 5/7a, (d)5/7b, (e)4/8a, (f) 4/8b, and (g) 8/8b GB<sub>SV</sub>.



Figure S11. Competing HER free energies for GB<sub>SV</sub> systems.

#### REFERENCES

- M. Mikkelsen, M. Jørgensen, and F. C. Krebs, "The teraton challenge. A review of fixation and transformation of carbon dioxide," *Energy Environ. Sci.*, vol. 3, no. 1, pp. 43-81, 2010, doi: 10.1039/b912904a.
- [2] B. Khezri, A. C. Fisher, and M. Pumera, "CO2 reduction: the quest for electrocatalytic materials," *Journal of Materials Chemistry A*, vol. 5, pp. 8230-8246, 2017.
- [3] Q. Lu and F. Jiao, "Electrochemical CO2 reduction: Electrocatalyst, reaction mechanism, and process engineering," *Nano Energy*, vol. 29, pp. 439-456, 2016.
- [4] L. Zhang, Z. J. Zhao, and J. Gong, "Nanostructured Materials for Heterogeneous Electrocatalytic CO2 Reduction and their Related Reaction Mechanisms," *Angew Chem Int Ed Engl*, vol. 56, no. 38, pp. 11326-11353, Sep 11 2017, doi: 10.1002/anie.201612214.
- Y. Xie *et al.*, "Reaction mechanisms for reduction of CO2 to CO on monolayer MoS2,"
   *Applied Surface Science*, vol. 499, no. 143964, 2020.
- [6] J. Qiao, Y. Liu, and J. Zhang, *Electrochemical reduction of carbon dioxide : fundamentals and technologies*, Boca Raton: CRC Press, 2016. [Online]. Available: <u>http://www.crcnetbase.com/isbn/9781482258257</u>.
- Z. Sun, T. Ma, H. Tao, Q. Fan, and B. Han, "Fundamentals and Challenges of Electrochemical CO2 Reduction Using Two-Dimensional Materials," *Chem*, vol. 3, no. 4, pp. 560-587, 2017, doi: 10.1016/j.chempr.2017.09.009.
- [8] Y. Fang, X. Cheng, J. C. Flake, and Y. Xu, "CO2 electrochemical reduction at thiolatemodified bulk Au electrodes," *Catalysis Science & Technology*, vol. 9, no. 10, pp. 2689-2701, 2019, doi: 10.1039/c9cy00506d.

- [9] D.-R. Yang *et al.*, "Importance of Au nanostructures in CO2 electrochemical reduction reaction," *Science Bulletin*, vol. 65, no. 10, pp. 796-802, 2020, doi: 10.1016/j.scib.2020.01.015.
- [10] W. Zhu *et al.*, "Monodisperse Au nanoparticles for selective electrocatalytic reduction of CO2 to CO," *J Am Chem Soc*, vol. 135, no. 45, pp. 16833-6, Nov 13 2013, doi: 10.1021/ja409445p.
- [11] H. Xie, T. Wang, J. Liang, Q. Li, and S. Sun, "Cu-based nanocatalysts for electrochemical reduction of CO2," *Nano Today*, vol. 21, pp. 41-54, 2018, doi: 10.1016/j.nantod.2018.05.001.
- [12] A. J. Garza, A. T. Bell, and M. Head-Gordon, "Mechanism of CO2 Reduction at Copper Surfaces: Pathways to C2 Products," *ACS Catalysis*, vol. 8, no. 2, pp. 1490-1499, 2018, doi: 10.1021/acscatal.7b03477.
- [13] X. Wang *et al.*, "Mechanistic reaction pathways of enhanced ethylene yields during electroreduction of CO2-CO co-feeds on Cu and Cu-tandem electrocatalysts," *Nat Nanotechnol*, vol. 14, no. 11, pp. 1063-1070, Nov 2019, doi: 10.1038/s41565-019-0551-6.
- [14] S. Nitopi *et al.*, "Progress and Perspectives of Electrochemical CO2 Reduction on Copper in Aqueous Electrolyte," *Chem Rev*, vol. 119, no. 12, pp. 7610-7672, Jun 26 2019, doi: 10.1021/acs.chemrev.8b00705.
- [15] X. Yuan *et al.*, "Interface Engineering of Silver-Based Heterostructures for CO2 Reduction Reaction," *ACS Appl Mater Interfaces*, vol. 12, no. 50, pp. 56642-56649, Dec 16 2020, doi: 10.1021/acsami.0c19031.

- [16] S. Liu *et al.*, "Shape-Dependent Electrocatalytic Reduction of CO2 to CO on Triangular Silver Nanoplates," *J Am Chem Soc*, vol. 139, no. 6, pp. 2160-2163, Feb 15 2017, doi: 10.1021/jacs.6b12103.
- [17] Q. He *et al.*, "Accelerating CO2 Electroreduction to CO Over Pd Single-Atom Catalyst,"
   *Advanced Functional Materials*, vol. 30, no. 17, 2020, doi: 10.1002/adfm.202000407.
- [18] Q. Chang *et al.*, "Boosting Activity and Selectivity of CO2 Electroreduction by Pre-Hydridizing Pd Nanocubes," *Small*, vol. 16, no. 49, p. e2005305, Dec 2020, doi: 10.1002/smll.202005305.
- [19] H. Liu, J. Liu, and B. Yang, "Computational insights into the strain effect on the electrocatalytic reduction of CO2 to CO on Pd surfaces," *Phys Chem Chem Phys*, vol. 22, no. 17, pp. 9600-9606, May 6 2020, doi: 10.1039/d0cp01042a.
- [20] D. L. T. Nguyen, Y. Kim, Y. J. Hwang, and D. H. Won, "Progress in development of electrocatalyst for CO2 conversion to selective CO production," *Carbon Energy*, vol. 2, pp. 72-98, 2020.
- [21] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, and A. Kis, "2D transition metal dichalcogenides," *Nature Reviews Materials*, vol. 2, no. 8, p. 17033, 2017/06/13 2017, doi: 10.1038/natrevmats.2017.33.
- [22] K. Kang, S. Chen, and E.-H. Yang, "12 Synthesis of transition metal dichalcogenides," in Synthesis, Modeling, and Characterization of 2D Materials, and Their Heterostructures, E.-H. Yang, D. Datta, J. Ding, and G. Hader Eds.: Elsevier, 2020, pp. 247-264.

- [23] M. Asadi *et al.*, "Nanostructured transition metal dichalcogenide electrocatalysts for CO<sub>2</sub> reduction in ionic liquid," *Science*, vol. 353, no. 6298, pp. 467-470, 2016, doi: 10.1126/science.aaf4767.
- [24] J. Pan, R. Wang, X. Xu, J. Hu, and L. Ma, "Transition metal doping activated basal-plane catalytic activity of two-dimensional 1T'-ReS2 for hydrogen evolution reaction: a firstprinciples calculation study," *Nanoscale*, 10.1039/C9NR00997C vol. 11, no. 21, pp. 10402-10409, 2019, doi: 10.1039/C9NR00997C.
- [25] X. Liu *et al.*, "Highly Active, Durable Ultrathin MoTe2 Layers for the Electroreduction of CO2 to CH4," *Small*, vol. 14, no. 16, p. 1704049, 2018, doi: https://doi.org/10.1002/smll.201704049.
- [26] J. Cavin *et al.*, "2D High-Entropy Transition Metal Dichalcogenides for Carbon Dioxide Electrocatalysis," *Advanced Materials*, vol. 33, no. 31, p. 2100347, 2021, doi: https://doi.org/10.1002/adma.202100347.
- [27] X. Li, S. Wang, L. Li, X. Zu, Y. Sun, and Y. Xie, "Opportunity of Atomically Thin Two-Dimensional Catalysts for Promoting CO2 Electroreduction," *Accounts of Chemical Research*, vol. 53, no. 12, pp. 2964-2974, 2020/12/15 2020, doi: 10.1021/acs.accounts.0c00626.
- [28] K. Chan, C. Tsai, H. A. Hansen, and J. K. Nørskov, "Molybdenum Sulfides and Selenides as Possible Electrocatalysts for CO2 Reduction," *ChemCatChem*, vol. 6, no. 7, pp. 1899-1905, 2014, doi: <u>https://doi.org/10.1002/cctc.201402128</u>.
- [29] M. Asadi *et al.*, "Robust carbon dioxide reduction on molybdenum disulphide edges," *Nature Communications*, vol. 5, no. 1, p. 4470, 2014.
- [30] P. Abbasi *et al.*, "Tailoring the Edge Structure of Molybdenum Disulfide toward Electrocatalytic Reduction of Carbon Dioxide," *ACS Nano*, vol. 11, no. 1, pp. 453-460, 2017/01/24 2017, doi: 10.1021/acsnano.6b06392.
- [31] H. Li *et al.*, "Edge-Exposed Molybdenum Disulfide with N-Doped Carbon
   Hybridization: A Hierarchical Hollow Electrocatalyst for Carbon Dioxide Reduction,"
   Advanced Energy Materials, vol. 9, no. 18, 2019, doi: 10.1002/aenm.201900072.
- [32] A. N. Mehta *et al.*, "Grain-Boundary-Induced Strain and Distortion in Epitaxial Bilayer MoS2 Lattice," *J. Phys. Chem. C*, vol. 124, no. 11, pp. 6472-6478, 2020.
- [33] M. Upmanyu, D. J. Srolovitz, L. S. Shvindlerman, and G. Gottstein, "Vacancy Generation During Grain Boundary Migration," *INTERFACE SCIENCE 6*, pp. 287-298, 1998.
- [34] "Statistical Review of World Energy." [Online]. Available: https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energyeconomics/statistical-review/bp-stats-review-2020-fullreport.pdf?utm\_source=BP\_Global\_GroupCommunications\_UK\_external&utm\_medium =email&utm\_campaign=11599394\_Statistical%20Review%202020%20-%20on%20the %20day%20reminder&dm\_i=1PGC%2C6WM5E%2COV0LQ4%2CRQW75%2C1
- [35] X. Liu *et al.*, "pH effects on the electrochemical reduction of CO(2) towards C2 products on stepped copper," *Nature Communications*, vol. 10, no. 1, p. 32, 2019/01/03 2019, doi: 10.1038/s41467-018-07970-9.
- [36] A. S. Varela *et al.*, "pH Effects on the Selectivity of the Electrocatalytic CO2 Reduction on Graphene-Embedded Fe–N–C Motifs: Bridging Concepts between Molecular

Homogeneous and Solid-State Heterogeneous Catalysis," *ACS Energy Letters*, vol. 3, no.4, pp. 812-817, 2018, doi: 10.1021/acsenergylett.8b00273.

- [37] A. S. Varela, "The importance of pH in controlling the selectivity of the electrochemical CO2 reduction," *Current Opinion in Green and Sustainable Chemistry*, vol. 26, p. 100371, 2020/12/01/ 2020, doi: <u>https://doi.org/10.1016/j.cogsc.2020.100371</u>.
- [38] T. Mizuno, K. Ohta, A. Sasaki, T. Akai, M. Hirano, and A. Kawabe, "Effect of Temperature on Electrochemical Reduction of High-Pressure CO2 with In, Sn, and Pb Electrodes," *Energy Sources*, vol. 17, no. 5, pp. 503-508, 1995/09/01 1995, doi: 10.1080/00908319508946098.
- [39] L. Wang *et al.*, "Electrochemical Carbon Monoxide Reduction on Polycrystalline Copper: Effects of Potential, Pressure, and pH on Selectivity toward Multicarbon and Oxygenated Products," *ACS Catalysis*, vol. 8, no. 8, pp. 7445-7454, 2018/08/03 2018, doi: 10.1021/acscatal.8b01200.
- [40] C. I. Shaughnessy *et al.*, "Intensified Electrocatalytic CO2 Conversion in Pressure-Tunable CO2 -Expanded Electrolytes," *ChemSusChem*, vol. 12, no. 16, pp. 3761-3768, Aug 22 2019, doi: 10.1002/cssc.201901107.
- [41] Y. Xu *et al.*, "Oxygen-tolerant electroproduction of C2 products from simulated flue gas," *Energy & Environmental Science*, vol. 13, no. 2, pp. 554-561, 2020, doi: 10.1039/c9ee03077h.
- [42] M. Moura de Salles Pupo and R. Kortlever, "Electrolyte Effects on the Electrochemical Reduction of CO2," *ChemPhysChem*, vol. 20, no. 22, pp. 2926-2935, 2019, doi: <u>https://doi.org/10.1002/cphc.201900680</u>.

- [43] M. König, J. Vaes, E. Klemm, and D. Pant, "Solvents and Supporting Electrolytes in the Electrocatalytic Reduction of CO2," *iScience*, vol. 19, pp. 135-160, 2019/09/27/ 2019, doi: <u>https://doi.org/10.1016/j.isci.2019.07.014</u>.
- [44] M. R. Singh, J. D. Goodpaster, A. Z. Weber, M. Head-Gordon, and A. T. Bell,
  "Mechanistic insights into electrochemical reduction of CO2 over Ag using density
  functional theory and transport models," *Proc Natl Acad Sci U S A*, vol. 114, no. 42, pp.
  E8812-E8821, Oct 17 2017, doi: 10.1073/pnas.1713164114.
- [45] G. O. Larrazábal, M. Ma, and B. Seger, "A Comprehensive Approach to Investigate CO2 Reduction Electrocatalysts at High Current Densities," *Accounts of Materials Research*, vol. 2, no. 4, pp. 220-229, 2021/04/23 2021, doi: 10.1021/accountsmr.1c00004.
- [46] C. B. Hiragond, H. Kim, J. Lee, S. Sorcar, C. Erkey, and S.-I. In, "Electrochemical CO2 Reduction to CO Catalyzed by 2D Nanostructures," *Catalysts*, vol. 10, no. 1, p. 98, 2020.
   [Online]. Available: https://www.mdpi.com/2073-4344/10/1/98.
- [47] H. Chen *et al.*, "Catalytic Effect on CO2 Electroreduction by Hydroxyl-Terminated Two-Dimensional MXenes," *ACS Applied Materials & Interfaces*, vol. 11, no. 40, pp. 36571-36579, 2019/10/09 2019, doi: 10.1021/acsami.9b09941.
- [48] A. D. Handoko, K. H. Khoo, T. L. Tan, H. Jin, and Z. W. Seh, "Establishing new scaling relations on two-dimensional MXenes for CO2 electroreduction," *Journal of Materials Chemistry A*, 10.1039/C8TA06567E vol. 6, no. 44, pp. 21885-21890, 2018, doi: 10.1039/C8TA06567E.
- Y. Xiao and W. Zhang, "High throughput screening of M3C2 MXenes for efficient CO2 reduction conversion into hydrocarbon fuels," *Nanoscale*, vol. 12, no. 14, pp. 7660-7673, 2020, doi: 10.1039/c9nr10598k.

- [50] A. D. Handoko, H. Chen, Y. Lum, Q. Zhang, B. Anasori, and Z. W. Seh, "Two-Dimensional Titanium and Molybdenum Carbide MXenes as Electrocatalysts for CO2 Reduction," *iScience*, vol. 23, no. 6, p. 101181, 2020/06/26/ 2020, doi: https://doi.org/10.1016/j.isci.2020.101181.
- [51] N. Li *et al.*, "Understanding of Electrochemical Mechanisms for CO2 Capture and Conversion into Hydrocarbon Fuels in Transition-Metal Carbides (MXenes)," *ACS Nano*, vol. 11, no. 11, pp. 10825-10833, 2017/11/28 2017, doi: 10.1021/acsnano.7b03738.
- [52] F. Yang *et al.*, "Bismuthene for highly efficient carbon dioxide electroreduction reaction," *Nature Communications*, vol. 11, no. 1, p. 1088, 2020/02/27 2020, doi: 10.1038/s41467-020-14914-9.
- Y. Wang, X. Zhu, and Y. Li, "Spin–Orbit Coupling-Dominated Catalytic Activity of Two-Dimensional Bismuth toward CO2 Electroreduction: Not the Thinner the Better," *The Journal of Physical Chemistry Letters*, vol. 10, no. 16, pp. 4663-4667, 2019/08/15 2019, doi: 10.1021/acs.jpclett.9b01406.
- [54] J. Xu *et al.*, "Carbon Dioxide Electroreduction into Syngas Boosted by a Partially Delocalized Charge in Molybdenum Sulfide Selenide Alloy Monolayers," *Angewandte Chemie International Edition*, vol. 56, no. 31, pp. 9121-9125, 2017, doi: 10.1002/anie.201704928.
- [55] H. Li *et al.*, "Edge-Exposed Molybdenum Disulfide with N-Doped Carbon Hybridization: A Hierarchical Hollow Electrocatalyst for Carbon Dioxide Reduction," *Advanced Energy Materials*, vol. 9, no. 18, p. 1900072, 2019, doi:

https://doi.org/10.1002/aenm.201900072.

- [56] X. Hong, K. Chan, C. Tsai, and J. K. Nørskov, "How Doped MoS2 Breaks Transition-Metal Scaling Relations for CO2 Electrochemical Reduction," *ACS Catalysis*, vol. 6, no. 7, pp. 4428-4437, 2016/07/01 2016, doi: 10.1021/acscatal.6b00619.
- Y. Ji, J. K. Nørskov, and K. Chan, "Scaling Relations on Basal Plane Vacancies of Transition Metal Dichalcogenides for CO2 Reduction," *The Journal of Physical Chemistry C*, vol. 123, no. 7, pp. 4256-4261, 2019/02/21 2019, doi: 10.1021/acs.jpcc.8b11628.
- [58] T. He, K. Reuter, and A. Du, "Atomically dispersed asymmetric Cu–B pair on 2D carbon nitride synergistically boosts the conversion of CO into C2 products," *Journal of Materials Chemistry A*, 10.1039/C9TA12090D vol. 8, no. 2, pp. 599-606, 2020, doi: 10.1039/C9TA12090D.
- [59] X. Cui, W. An, X. Liu, H. Wang, Y. Men, and J. Wang, "C2N-graphene supported single-atom catalysts for CO2 electrochemical reduction reaction: mechanistic insight and catalyst screening," *Nanoscale*, 10.1039/C8NR04961K vol. 10, no. 32, pp. 15262-15272, 2018, doi: 10.1039/C8NR04961K.
- [60] A. M. Verma, K. Honkala, and M. M. Melander, "Computational Screening of Doped Graphene Electrodes for Alkaline CO2 Reduction," (in English), *Frontiers in Energy Research*, Original Research vol. 8, no. 388, 2021-February-02 2021, doi: 10.3389/fenrg.2020.606742.
- [61] Y.-L. Qiu, H.-X. Zhong, T.-T. Zhang, W.-B. Xu, X.-F. Li, and H.-M. Zhang, "Copper Electrode Fabricated via Pulse Electrodeposition: Toward High Methane Selectivity and Activity for CO2 Electroreduction," *ACS Catalysis*, vol. 7, no. 9, pp. 6302-6310, 2017/09/01 2017, doi: 10.1021/acscatal.7b00571.

- [62] A. Liu, W. Guan, K. Wu, X. Ren, L. Gao, and T. Ma, "Density functional theory study of nitrogen-doped graphene as a high-performance electrocatalyst for CO2RR," *Applied Surface Science*, vol. 540, p. 148319, 2021/02/28/ 2021, doi: https://doi.org/10.1016/j.apsusc.2020.148319.
- [63] N. Zhang, M. I. Hussain, M. Xia, and C. Ge, "Graphitic Carbon Nitride Nanosheets-Immobilized Single-Atom Zn Towards Efficient Electroreduction of CO2," *Nano*, vol. 16, no. 02, p. 2150016, 2021, doi: 10.1142/s1793292021500168.
- [64] J. Zhang, J. Wang, Z. Wu, S. Wang, Y. Wu, and X. Liu, "Heteroatom (Nitrogen/Sulfur) Doped Graphene as an Efficient Electrocatalyst for Oxygen Reduction and Evolution
   Reactions," *Catalysts*, vol. 8, p. 475, 10/19 2018, doi: 10.3390/catal8100475.
- [65] X. Lu, T. H. Tan, Y. H. Ng, and R. Amal, "Highly Selective and Stable Reduction of CO2 to CO by a Graphitic Carbon Nitride/Carbon Nanotube Composite Electrocatalyst," *Chemistry – A European Journal*, vol. 22, no. 34, pp. 11991-11996, 2016, doi: <u>https://doi.org/10.1002/chem.201601674</u>.
- [66] K. Jiang *et al.*, "Isolated Ni single atoms in graphene nanosheets for high-performance CO2 reduction," *Energy & Environmental Science*, 10.1039/C7EE03245E vol. 11, no. 4, pp. 893-903, 2018, doi: 10.1039/C7EE03245E.
- [67] N. Sreekanth, M. A. Nazrulla, T. V. Vineesh, K. Sailaja, and K. L. Phani, "Metal-free boron-doped graphene for selective electroreduction of carbon dioxide to formic acid/formate," *Chemical communications (Cambridge, England)*, vol. 51, no. 89, pp. 16061-4, 2015, doi: 10.1039/c5cc06051f.
- [68] Y. Wang, J. Chen, G. Wang, Y. Li, and Z. Wen, "Perfluorinated Covalent Triazine Framework Derived Hybrids for the Highly Selective Electroconversion of Carbon

Dioxide into Methane," *Angewandte Chemie International Edition*, vol. 57, no. 40, pp. 13120-13124, 2018, doi: <u>https://doi.org/10.1002/anie.201807173</u>.

- [69] X. Wang *et al.*, "Theoretical investigation on graphene-supported single-atom catalysts for electrochemical CO2 reduction," *Catalysis Science & Technology*, 10.1039/D0CY01870H vol. 10, no. 24, pp. 8465-8472, 2020, doi: 10.1039/D0CY01870H.
- S. Siahrostami, K. Jiang, M. Karamad, K. Chan, H. Wang, and J. Nørskov, "Theoretical Investigations into Defected Graphene for Electrochemical Reduction of CO2," ACS Sustainable Chemistry & Engineering, vol. 5, no. 11, pp. 11080-11085, 2017/11/06 2017, doi: 10.1021/acssuschemeng.7b03031.
- [71] Z. Chen *et al.*, "Tuning local carbon active sites saturability of graphitic carbon nitride to boost CO2 electroreduction towards CH4," *Nano Energy*, vol. 73, p. 104833, 2020/07/01/2020, doi: <u>https://doi.org/10.1016/j.nanoen.2020.104833</u>.
- [72] X. Sun *et al.*, "Design of a Cu(i)/C-doped boron nitride electrocatalyst for efficient conversion of CO2 into acetic acid," *Green Chemistry*, 10.1039/C7GC00503B vol. 19, no. 9, pp. 2086-2091, 2017, doi: 10.1039/C7GC00503B.
- [73] X. Tan, H. A. Tahini, H. Arandiyan, and S. C. Smith, "Electrocatalytic Reduction of Carbon Dioxide to Methane on Single Transition Metal Atoms Supported on a Defective Boron Nitride Monolayer: First Principle Study," *Advanced Theory and Simulations*, vol. 2, no. 3, p. 1800094, 2019, doi: <u>https://doi.org/10.1002/adts.201800094</u>.
- [74] S. Tang *et al.*, "Metal-Free Boron Nitride Nanoribbon Catalysts for Electrochemical CO2 Reduction: Combining High Activity and Selectivity," *ACS Applied Materials & Interfaces*, vol. 11, no. 1, pp. 906-915, 2019/01/09 2019, doi: 10.1021/acsami.8b18505.

- [75] X. Mao *et al.*, "Metal-free graphene/boron nitride heterointerface for CO2 reduction: Surface curvature controls catalytic activity and selectivity," *EcoMat*, vol. 2, no. 1, p. e12013, 2020, doi: <u>https://doi.org/10.1002/eom2.12013</u>.
- [76] L. Majidi *et al.*, "2D Copper Tetrahydroxyquinone Conductive Metal–Organic
   Framework for Selective CO2 Electrocatalysis at Low Overpotentials," *Advanced Materials*, vol. 33, no. 10, p. 2004393, 2021, doi:
   https://doi.org/10.1002/adma.202004393.
- [77] A. S. Varela Gasque, W. Ju, and P. Strasser, "Molecular Nitrogen-Carbon Catalysts, Solid Metal Organic Framework Catalysts, and Solid Metal/Nitrogen-Doped Carbon (MNC) Catalysts for the Electrochemical CO 2 Reduction," *Advanced Energy Materials*, vol. 8, p. 1802905, 10/01 2018, doi: 10.1002/aenm.201802905.
- [78] H. Zhong *et al.*, "Synergistic electroreduction of carbon dioxide to carbon monoxide on bimetallic layered conjugated metal-organic frameworks," *Nature Communications*, vol. 11, no. 1, p. 1409, 2020/03/16 2020, doi: 10.1038/s41467-020-15141-y.
- [79] Z. Dong *et al.*, "Raman Characterization on Two-Dimensional Materials-Based Thermoelectricity," *Molecules*, vol. 24, p. 88, 12/27 2018, doi: 10.3390/molecules24010088.
- [80] Hiragond, Ali, and Sorcar, "Hierarchical Nanostructured Photocatalysts for CO2 Photoreduction," *Catalysts*, vol. 9, p. 370, 2019.
- [81] M. G. Kibria *et al.*, "Electrochemical CO2 Reduction into Chemical Feedstocks: From Mechanistic Electrocatalysis Models to System Design," *Advanced Materials*, vol. 31, no. 31, p. 1807166, 2019, doi: <u>https://doi.org/10.1002/adma.201807166</u>.

- [82] D. Ren, J. Fong, and B. S. Yeo, "The effects of currents and potentials on the selectivities of copper toward carbon dioxide electroreduction," *Nature Communications*, vol. 9, no. 1, p. 925, 2018/03/02 2018, doi: 10.1038/s41467-018-03286-w.
- [83] R. B. Sandberg, J. H. Montoya, K. Chan, and J. K. Nørskov, "CO-CO coupling on Cu facets: Coverage, strain and field effects," *Surface Science*, vol. 654, pp. 56-62, 2016/12/01/ 2016, doi: <u>https://doi.org/10.1016/j.susc.2016.08.006</u>.
- [84] J. H. Montoya, C. Shi, K. Chan, and J. K. Nørskov, "Theoretical Insights into a CO Dimerization Mechanism in CO2 Electroreduction," *The Journal of Physical Chemistry Letters*, vol. 6, no. 11, pp. 2032-2037, 2015/06/04 2015, doi: 10.1021/acs.jpclett.5b00722.
- [85] K. Jiang *et al.*, "Metal ion cycling of Cu foil for selective C–C coupling in electrochemical CO2 reduction," *Nature Catalysis*, vol. 1, no. 2, pp. 111-119, 2018/02/01 2018, doi: 10.1038/s41929-017-0009-x.
- [86] S. Ringe *et al.*, "Understanding Cation Effects in Electrochemical CO 2 Reduction," *Energy & Environmental Science*, vol. 12, pp. 3001-3014, 07/03 2019, doi: 10.1039/C9EE01341E.
- [87] Y. L. Ziyun Wang, Jacob Boes, Ying Wang, Edward Sargent. (2020). CO2Electrocatalyst Design Using Graph Theory.
- [88] M. Javaid, S. P. Russo, K. Kalantar-Zadeh, A. D. Greentree, and D. W. Drumm, "Band structure and giant Stark effect in two-dimensional transition-metal dichalcogenides," *Electronic Structure*, vol. 1, no. 1, p. 015005, 2018/11/20 2018, doi: 10.1088/2516-1075/aadf44.

- [89] B. Hammer and J. K. Norskov, "Why gold is the noblest of all the metals," *Nature*, vol. 376, no. 6537, pp. 238-240, 1995/07/01 1995, doi: 10.1038/376238a0.
- [90] J. K. Nørskov, F. Abild-Pedersen, F. Studt, and T. Bligaard, "Density functional theory in surface chemistry and catalysis," *Proceedings of the National Academy of Sciences*, vol. 108, no. 3, pp. 937-943, 2011, doi: 10.1073/pnas.1006652108.
- [91] L. G. M. Pettersson and A. Nilsson, "A Molecular Perspective on the d-Band Model: Synergy Between Experiment and Theory," *Topics in Catalysis*, vol. 57, no. 1, pp. 2-13, 2014/02/01 2014, doi: 10.1007/s11244-013-0157-4.
- [92] G. Kresse and J. Hafner, "Norm-conserving and ultrasoft pseudopotentials for first-row and transition elements," *Journal of Physics: Condensed Matter*, vol. 6, no. 40, pp. 8245-8257, 1994/10/03 1994, doi: 10.1088/0953-8984/6/40/015.
- [93] G. Kresse and D. Joubert, "From ultrasoft pseudopotentials to the projector augmented-wave method," *Physical Review B*, vol. 59, no. 3, pp. 1758-1775, 01/15/1999, doi: 10.1103/PhysRevB.59.1758.
- [94] G. Kresse and J. Hafner, "Ab initio molecular dynamics for liquid metals," *Physical Review B*, vol. 47, no. 1, pp. 558-561, 01/01/1993, doi: 10.1103/PhysRevB.47.558.
- [95] G. Kresse and J. Furthmüller, "Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set," *Computational Materials Science*, vol. 6, no. 1, pp. 15-50, 1996/07/01/ 1996, doi: <u>https://doi.org/10.1016/0927-0256(96)00008-0</u>.
- [96] G. Kresse and J. Furthmüller, "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set," *Physical Review B*, vol. 54, no. 16, pp. 11169-11186, 10/15/1996, doi: 10.1103/PhysRevB.54.11169.

- [97] S. Grimme, "Semiempirical GGA-type density functional constructed with a long-range dispersion correction," *Journal of Computational Chemistry*, vol. 27, no. 15, pp. 1787-1799, 2006, doi: <u>https://doi.org/10.1002/jcc.20495</u>.
- [98] Y. Chen, P. Ou, X. Bie, and J. Song, "Basal plane activation in monolayer MoTe2 for the hydrogen evolution reaction via phase boundaries," *Journal of Materials Chemistry A*, 10.1039/D0TA06165D vol. 8, no. 37, pp. 19522-19532, 2020, doi: 10.1039/D0TA06165D.
- [99] D. J. Lavrich, S. M. Wetterer, S. L. Bernasek, and G. Scoles, "Physisorption and Chemisorption of Alkanethiols and Alkyl Sulfides on Au(111)," *J. Phys. Chem. B*, vol. 102, no. 18, pp. 3456-3465, 1998.
- B. Huang, L. Xiao, J. Lu, and L. Zhuang, "Spatially Resolved Quantification of the Surface Reactivity of Solid Catalysts " *Angewandte Chemie International Edition*, vol. 55, pp. 6239–6243, 2016.