Discovering Novel Materials for Smart Windows via First-Principles Calculations

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Discovering Novel Materials for Smart Windows via First-Principles Calculations

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STATEMENT

This work has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due references is made in the thesis itself.

Signature of Candidate

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Date: 25/03/2022

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This thesis was completed with the help of many professional and enthusiastic people, who are very special to me.

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My sincere appreciation also goes to my co-principal supervisor A./Prof. Tim Gould, for his guidance and support at all critical moments. His rigorous academic attitude and diligent work style are my role models.

Additionally, I wish to dedicate my heartfelt thanks to my external supervisor Prof. Feng Pan, for getting me started in first-principles calculations. Communications with him have greatly broadened my research ideas, which has long-term benefits.

Meanwhile, the support and guidance from the following people are highly appreciated. They are Ms. Jenny, Prof. Yinghuai Qiang, Dr. Mouyi Weng, A./Prof. Yun Wang, Dr. David Adekoya, Dr. Hao Chen, Mr. Kelin He, Dr. Luke Hence, Mr. Zimo Huang, Dr. Lixue Jiang, Dr. Han Yeu Ling, Dr. Junxian Liu, Mr. Shangshu Qian, Dr. Zhong Su, Mr. Yuhui Tian, Dr. Yazhou Wang, Dr. Zhenzhen Wu, Mr. Chao Xing and his wife Ms. Shuo Qi, Dr. Ding Yuan, Dr. Yubai Zhang, Ms. Mengting Zheng, Dr. Ming Zhou, Ms. Yuxuan Zhu, and Dr. Meng Zu.

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Many thanks to all the staff and colleagues in ENV, ESC, CCCE, and GGRS, especially Dr. Mohammad Al-Mamun, A./Prof. Porun Liu, Ms. Christina Perry, and Ms. Joanne Umemoto. The financial support from Australian Government and Griffith University is greatly appreciated.

Last but not least, I would like to express my eternal gratefulness and love to my parents, my wife, and my children, who mean the world to me.

TABLE OF CONTENTS

ACRONYMS

BHT	Benzenehexathiol
BSE	Bethe-Salpeter equation
CB	Conduction band
CBM	Conduction band minimum
CE	Coloration efficiency
COF	Covalent organic framework
COHP	Crystal orbital Hamilton population
CONASHs	Coordination nanosheets
CR	Contrast ratio
DFT	Density functional theory
DOS	Density of states
ECD	Electrochromic device
ELF	Electron localization functions
GGA	Generalized gradient approximation
HER	Hydrogen evolution reaction
HSE	Heyd-Scuseria-Ernzerhof
IPA	Independent particle approximation
LTO	$Li_4Ti_5O_{12}$
MBPT	Many-body perturbation theory
MIR	Mid-infrared spectrum
MOF	Metal-organic frameworks
PAW	Projector augmented wave
PBE	Perdew-Burke-Ernzerhof

TM	Transition metal
VASP	Vienna *ab initio* Simulation Package
VB	Valence band
VBM	Valence band maximum
2D	Two-dimensional
-IpCOHP	Negative integrated projected crystal orbital Hamilton population

PUBLICATIONS

Acknowledgment of Papers included in this Thesis

Section 9.1 of the Griffith University Code for the Responsible Conduct of Research ("Criteria for Authorship"), in accordance with Section 5 of the Australian Code for the Responsible Conduct of Research, states:

> To be named as an author, a researcher must have made a substantial scholarly contribution to the creative or scholarly work that constitutes the research output and be able to take public responsibility for at least that part of the work they contributed. Attribution of authorship depends to some extent on the discipline and publisher policies, but in all cases, authorship must be based on substantial contributions in a combination of one or more of:
>
> - Conception and design of the research project
> - Analysis and interpretation of research data
> - Drafting or making significant parts of the creative or scholarly work or critically revising it so as to contribute significantly to the final output.

Section 9.3 of the Griffith University Code ("Responsibilities of Researchers"), in accordance with Section 5 of the Australian Code, states:

> Researchers are expected to:
>
> - Offer authorship to all people, including research trainees, who meet the criteria for authorship listed above, but only those people.
> - Accept or decline offers of authorship promptly in writing.
> - Include in the list of authors only those who have accepted authorship
> - Appoint one author to be the executive author to record authorship and manage correspondence about the work with the publisher and other interested parties.
> - Acknowledge all those who have contributed to the research, facilities, or materials but who do not qualify as authors, such as research assistants, technical staff, and advisors on cultural or community knowledge. Obtain written consent to name individuals.

Chapter Publications

This thesis consists of one published paper from Chapter 3, and four submitted or submission-ready manuscripts of Chapters 2, 4, 5, and 6. My contribution to each co-authored paper is outlined at the front of the relevant chapter.

(Note IF: Impact factor 2020)

Chapter 2:

Li, M., Wu, Z., Gould, T., Zhang, S. Unconventional two-dimensional electrochromic materials: achievements and future challenges. (to be submitted as a review paper)

Chapter 3:

Li, M., Gould, T., Zhong, S., Li, S., Pan, F., Zhang, S. Electrochromic properties of $Li_4Ti_5O_{12}$: from visible to infrared spectrum. ***Applied Physics Letters*** 2019, 115, 073902 (IF:3.791)

Chapter 4:

Li, M., Tian, Y., Wu, Z., Li, S., Pan, F., Gould, T., Zhang, S. Theoretical investigation on the lithium intercalation-induced electrochromic properties of TiS_2 nanosheets. (submitted to ***Journal of Physical Chemistry C, being resised***)

Chapter 5:

Li, M., Wu, Z., Chen, H., Gould, T., Zhang, S. First-principles exploration of two-dimensional benzenehexathiolate coordination nanosheets for broadband electrochromic devices. (submitted to ***Advanced Functional Materials, being revised***)

Chapter 6:

Li, M., Wu, Z., Tian, Y., Pan, F., Zhang, S., Gould, T. Band-structure engineering of copper benzenehexathiol for reversible mechanochromism: A first-principles study. (submitted to ***Journal of Physical Chemistry C***)

Appropriate acknowledgements of those who contributed to the research but did not qualify as authors are included in each paper.

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Meng Li

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Supervisor: Prof. Shanqing Zhang

Additional Relevant Publications

In addition to the published works that formed the research chapters of this thesis, other co-authored publications were directly relevant, but did not form part of the thesis itself.

1. Wu Z., **Li M. (Co-first Author)**, Tian Y., et al. Cyclohexanedodecol-assisted interfacial engineering for robust and high-performance zinc metal anode. ***Nano-Micro Letters*** 2022 (accepted) (IF: 16.419)
2. Wang Y., **Li M.**, Xu L., et al. Polar and conductive iron carbide@N-doped porous carbon nanosheets as a sulfur host for high performance lithium sulfur batteries. ***Chemical Engineering Journal*** 2019, 358, 962-968. (IF: 13.273)
3. Adekoya D., **Li M.**, Hankel M., et al. Design of a 1D/2D C_3N_4/rGO composite as an anode material for stable and effective potassium storage. ***Energy Storage Materials*** 2020, 25, 495-501. (IF: 17.789)
4. Liu H., Du C., **Li M.**, et al. One-Pot Hydrothermal Synthesis of SnO_2/BiOBr heterojunction photocatalysts for the efficient degradation of organic pollutants under visible light. ***ACS Applied Materials & Interfaces*** 2018, 10*,* 28686-28694. (IF: 9.229)
5. Zhong S., Han Y., **Li M.**, et al. Honeycomb-like carbon materials derived from coffee extract via a "salty" thermal treatment for high-performance Li-I_2 batteries. ***Carbon Energy***, 2020, 2, 265-275.
6. Zhong S., Liu J., **Li M.**, et al. Defect engineering in titanium-based oxides for electrochemical energy storage devices. ***Electrochemical Energy Reviews*** 2020, 3, 286-343. (IF: 28.905)
7. Tian Y., Li X., **Li M.**, et al. Interface engineering of CoS/CoO@N-doped graphene nanocomposite for high-performance rechargeable Zn–air batteries. ***Nano-Micro Letters*** 2021, 13, 3. (IF: 16.419)

ABSTRACT

Currently, achieving carbon neutrality is a historical global concern, including China 2060 and USA 2050, which refers to a dynamic balance between carbon emissions and carbon fixation. To address these concerns, human society is not only promoting the scale of artificial carbon sinks but also reducing carbon emissions. The latter plays a vital position in achieving carbon neutrality, necessitating high-efficiency energy consumption. Among the key drivers of energy consumption, buildings consume approximately 40%, more energy than the industry and transportation sectors. Half of building energy is used in ventilation and temperature control (heating and cooling for buildings), making it the largest unrealized cost-effective emission savings. The main reason is that traditional windows allow heat transfer in an undesirable direction that helps buildings gain heat in summer and release heat in winter. Moreover, the traditional daylighting control solutions, i.e., blinds, lead to the commonplace occurrence of closing blinds and lights on, with poor daylight utilization and more electric energy consumption. Smart windows, which can regulate illumination in buildings and heat exchange with the environment, are regarded as the ideal solution of this problem. The most widely used and investigated smart windows are based on electrochromism, with few researchers focusing on the unconventional ones based on mechanochromism.

Electrochromism refers to the reversible and persistent changes of colour, transmittance, or other optical properties through electrochemical redox reactions under applied voltages. A typical electrochromic device is essentially a battery with electrochromic materials as electrodes. Our first two research chapters report electrochromic effects in traditional inorganic anode and cathode materials, namely LTO and TiS_2, respectively. For LTO anode, we performed a detailed analysis of LTO's optical properties during charging/discharging via a robust study of the DFT. Our study suggests that the absorption of infrared light is highly

sensitive to lithium intercalation in the LTO lattice, in contrast to that of visible wavelengths. The electrochemical intercalation introduced donor states which gradually expanded and moved to deeper levels in the forbidden band, resulting in better conductivity and lower transmittance. For TiS_2 cathode, we theoretically explored structural, electronic, and electrochromic properties of bulk and monolayer TiS_2 nanosheets before and after lithium intercalation, using the most accurate available theoretical methods: SCAN+rVV10 for structures, *GW* for band gaps, COHP for bonding strength analysis, and IPA for optical properties in the solar spectrum. Our results suggest that during lithium intercalation/deintercalation, changes in lattice parameters, bandgap between S-*p* and Ti-*d*, and electrochromic properties are interlayer distance-dependent. For example, the modulation ranges of transmitted visible light for bulk and monolayer TiS_2 are 24-48% and 34-75%, respectively. These two work point out two factors affecting the electrochromic performance, namely donor states in the forbidden band and interlayer distances, which provide insights into the mechanism of electrochromism.

Besides traditional inorganic materials, CONASHs are an emerging group of 2D materials with unique physical and chemical properties in a wide range of applications, such as superconductivity, hydrogen evolution catalyst, chemical sensing, spintronic and thermoelectric devices. In the third research chapter, we screen out electrochromic materials in a series of TM-BHT via first-principles calculations. Meanwhile, during lithiation/delithiation, changes in lattice structures, atomic charges, bond strength, and electronic properties are explored in-depth. The incurred changes are then correlated with critical electrochromic properties. Our results show that Cu-BHT and Ag-BHT are the most promising broadband electrochromic materials for optical and thermal management in the wavelength range from

visible to mid-infrared. The theoretical guidance from this work paves a new path towards electrochromic applications of CONASHs that exploit the versatility of these 2D materials.

Further studies on Cu-BHT reveal the mechanochromic effect, due to the fragile balance of large-scale intralayer delocalization. In the fourth research chapter, we theoretically investigate atomic charges, bond length and strength, and electronic structures of Cu-BHT under uniaxial and biaxial strain. The mechanism of mechanochromic phenomenon is based on band-structure engineering, which is due to limited unoccupied states near the Fermi level for compressive strain and the broken π-d conjugated system for tensile strain. Both strains negatively affect electron conductivity. In terms of mechanochromic performance, Cu-BHT film achieves remarkable tunability in visible and near-infrared spectra under only 3% uniaxial and biaxial compressive strain, respectively. Corresponding modulation ranges are 2.7-74.6% and 0-87.6%, respectively. The strain-tuneable electronic properties of Cu-BHT provide it with great potential in smart windows, thermal camouflage, infrared radiative cooling, and various nanoscale electronic and optoelectronic applications.

In summary, we theoretically discover electrochromic and mechanochromic effect for smart windows in traditional inorganic materials and emerging CONASHs. Corresponding mechanism and induced changes in response to applied voltages or mechanical strain have been investigated in detail. The in-depth understanding of related eye-catching phenomena and newly discovered materials could not only promote field development, but also inspire more researchers to get involved.

CHAPTER 1

INTRODUCTION

1.1. SIGNIFICANCE OF THE PROJECT

Smart windows are able to regulate illumination in buildings and heat exchange with the environment in an elegant and dynamic way via switching between different states in transmittance in response to external stimuli. The most widely used and investigated smart windows is based on electrochromism, with few researchers focusing on the unconventional ones based on mechanochromism. Other applications for electrochromic and mechanochromic materials are displays, chameleonic fabric, electronic skin with tactile sensing, mechanical sensors, healthcare materials, and optical anticounterfeiting. Traditional electrochromic materials can be divided into inorganic materials, organic small molecules, conducting polymers, and metal complexes, with mechanochromic materials based on microscale wrinkles and nanovoids. However, their limited modulation ranges, slow switching speed, poor cycling stability and high materials cost still hinder their practical applications, which attracts an emerging scientific and technological interest in the exploration of new electrochromic and mechanochromic materials.

Searching for novel materials through large-scale experiments could be arduous and inefficient, even dependent on luck. First-principles calculations, on one hand, can deal with ideal stoichiometric compounds and undiscovered structures, in utter disregard of impurities, defects, and current existences. Moreover, screening large amounts of materials via computational tools is convenient, and the obtained results can be used for experimental verification, greatly accelerating research progress and saving huge amount of money, manpower, and time. On the other hand, benefiting from the rapid development of computing power and high-accuracy theories, theoretical calculations can provide results comparable to experiments in certain circumstances. Last but not least, first-principles calculations can provide fundamental and irreplaceable insights from views of electrons, occupying a vital position in mechanism

exploration. The above advantages have been clearly demonstrated in this project, with chapter 5 for materials screening, chapters 3,4,6 for theoretical property calculations for certain materials, and all these chapters for mechanism exploration. This project has exhibited the great power of first-principles calculations in the field of electrochromic and mechanochromic materials for smart windows.

1.2. RESEARCH OBJECTIVES

The central focus of this project is to discover novel electrochromic and mechanochromic materials, especially for smart windows. The specific objectives are as follows:

- To find undiscovered electrochromic effects among existing electrode materials and predict corresponding electrochromic properties.
- To screen a series of novel materials for possible electrochromic or mechanochromic devices with excellent properties.
- To discover unconventional materials with intrinsic mechanochromic effects, instead of microscale wrinkles and nanovoids.

1.3. THESIS OUTLINE

This thesis aims to provide further insights into existing and undiscovered materials in terms of electrochromism and mechanochromism. The thesis structure is shown as follows:

1) Chapter 1 highlights the significance of the project, proposes the search objectives, and outlines the framework of the thesis in relation to electrochromic and mechanochromic materials.
2) Chapter 2 provides a detailed literature review on unconventional two-dimensional electrochromic materials, namely covalent organic frameworks (COFs), coordination nanosheets (CONASHs), transition metal carbides/nitrides/carbonitrides (MXenes) and other materials.
3) Chapter 3 investigates the changes in optical properties and electronic structures of $Li_4Ti_5O_{12}$ before and after lithium insertion. The electrochromic mechanism and properties have been discussed in detail.
4) Chapter 4 theoretically predicts the lithium intercalation-induced electrochromic effect in widely known TiS_2 and compares calculated optical properties with experimental data.
5) Chapter 5 screens a series of transition metal benzenehexathiol (BHT) and predicts Cu-BHT and Ag-BHT as promising broadband electrochromic materials for optical devices and thermal management.
6) Chapter 6 discovers ultrasensitive mechanochromic effect in Cu-BHT based on band-structure engineering. The strain-induced changes in atomic charge, bond length and strength, and electronic structures are investigated in detail and correlated with critical mechanochromic properties.
7) Chapter 7 summarizes the complete text and raise the prospect for the future.

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CHAPTER 2

UNCONVENTIONAL TWO-DIMENSIONAL ELECTROCHROMIC MATERIALS: ACHIEVEMENTS AND FUTURE CHALLENGES

To be submitted as a review paper.

2.1. INTRODUCTORY REMARKS

This chapter includes one manuscript to be submitted as a review paper.

In this review, we systematically review the emerging groups of 2D electrochromic materials, namely covalent organic frameworks (COFs), coordination nanosheets (CONASHs), transition metal carbides/nitrides/carbonitrides (MXenes) and other materials. Our focus is on the relationship between their structures and performance. Finally, we propose future challenges for next-generation 2D electrochromic materials from the molecular level to the macro level. 2D Electrochromic materials will play crucial roles in the future, from emotional fulfillment to energy utilization.

2.2. STATEMENT OF CONTRIBUTION

This chapter includes one first-authored paper. The bibliographic details of the co-authored paper, including all authors, are:

Li Meng, Wu Zhenzhen, Gould Tim, and Shanqing Zhang

Recent advances in two-dimensional electrochromic materials

(To be submitted as a review paper)

My contribution to the paper involved:

Literature review, collection, and organization of information; preparation of manuscript.

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Name of Student: Meng Li

(Countersigned)_____(Date) 25/03/2022

Corresponding author of paper: Shanqing Zhang

(Countersigned)_____(Date) 25/03/2022

Supervisor: Shanqing Zhang

2.3. ARTICLE 1

CHAPTER 3

ELECTROCHROMIC PROPERTIES OF $Li_4Ti_5O_{12}$: FROM VISIBLE TO INFRARED SPECTRUM

Applied Physics Letters 2019, 115, 073902.

3.1. INTRODUCTORY REMARKS

The findings and development in this chapter were published in an article in ***Applied Physics Letters*** 2019, 115, 073902.

As a promising anode material, famous for its notable "zero-strain" characteristic, $Li_4Ti_5O_{12}$ (LTO) has experimentally shown a broadband electrochromic effect for applications like smart windows, thermal modulation, and infrared camouflage. However, a detailed understanding of the mechanisms responsible for these phenomena is still lacking. We fill this knowledge gap by analysing changes in optical properties of LTO in the electrochemical processes via a robust study of the density functional theory (DFT). Our results reveal that the absorption coefficient of infrared light is highly sensitive to the intercalated lithium in the LTO lattice, as opposed to that of visible light. This unique characteristic of LTO offers independent control of illumination and solar heat as smart windows. Furthermore, the DFT study also reveals that the electrochromic mechanism comes from the intercalated lithium-induced donor states in the band gap. The donor states will gradually expand and move to lower levels with further intercalation, resulting in better conductivity and poor transmittance, in line with the experimental observations.

3.2. STATEMENT OF CONTRIBUTION

This chapter includes one first-authored paper. The bibliographic details of the co-authored paper, including all authors, are:

Meng Li, Tim Gould, Zhong Su, Shunning Li, Feng Pan, and Shanqing Zhang.

Electrochromic properties of $Li_4Ti_5O_{12}$: from visible to infrared spectrum. ***Applied Physics Letters*** 2019, 115, 073902.

My contribution to the paper involved:

The theoretical experimental design and implementation; the collection and analysis of data; the preparation of the manuscript.

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Supervisor: Shanqing Zhang

3.3. ARTICLE 2

CHAPTER 4

THEORETICAL INVESTIGATION ON THE LITHIUM INTERCALATION-INDUCED ELECTROCHROMIC PROPERTIES OF TiS_2 NANOSHEETS

Submitted to Journal of Physical Chemistry C

4.1. INTRODUCTORY REMARKS

The findings and development in this chapter has been submitted to ***Journal of Physical Chemistry C***.

As the first lithium intercalation host proposed in 1976, TiS_2 nanosheets has been widely investigated both experimentally and theoretically for batteries and thermoelectric applications for over 40 years. The never-ending story of TiS_2 nanosheets has recently switched to its optical properties, such as optical limiting and photoelectric modulator. We report the electrochromic effect in TiS_2 nanosheets in detail, using the most accurate available theoretical methods. Specifically, the structural, electronic, and electrochromic properties of bulk and monolayer TiS_2 nanosheets before and after lithium intercalation have been investigated. Our results indicate that intercalation could increase lattice parameters and bandgap between S-*p* and Ti-*d*, especially for TiS_2 with larger interlayer distances. The electrochromic properties are also thickness-dependent, with a larger energetic modulation range of transmitted visible light. This work offers guidance on utilizing thickness-dependent characteristics of two-dimensional materials to hance electrochromic performance.

4.2. STATEMENT OF CONTRIBUTION

This chapter includes one first-authored paper. The bibliographic details of the co-authored paper, including all authors, are:

Meng Li, Yuhui Tian, Zhenzhen Wu, Shunning Li, Feng Pan, Tim Gould, and Shanqing Zhang. Theoretical investigation on the lithium intercalation-induced electrochromic properties of TiS_2 nanosheets. (Submitted to ***Journal of Physical Chemistry C***)

My contribution to the paper involved:

The theoretical experimental design and implementation; the collection and analysis of data; the preparation of the manuscript.

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Corresponding author of paper: Shanqing Zhang

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Supervisor: Shanqing Zhang

4.3. ARTICLE 3

CHAPTER 5
FIRST-PRINCIPLES EXPLORATION OF TWO-DIMENSIONAL BENZENEHEXATHIOLATE COORDINATION NANOSHEETS FOR BROADBAND ELECTROCHROMIC DEVICES

Submitted to Advanced Functional Materials

5.1. INTRODUCTORY REMARKS

The findings and development in this chapter has been submitted to ***Advanced Functional Materials***.

As an emerging group of two-dimensional (2D) materials, coordination nanosheets (CONASHs) have shown great diversities in a wide range of applications, due to their large specific surface area, unique electronic structures, and excellent electrochemical properties. Since the pioneer work done by Nishihara group in 2015, several electrochromic CONASHs have been synthesized. However, time-consuming and inefficient experiments for screening novel electrochromic CONASHs are still the bottleneck of their development. In this work, we theoretically investigated a series of transition metal benzenehexathiol (TM-BHT) via first-principles simulations, predicting Cu-BHT and Ag-BHT as promising broadband electrochromic materials for optical devices and thermal management. The lithium intercalation-induced changes in lattice structures, atomic charges, bond strength, electronic properties, and energy levels are explored and correlated with critical electrochromic properties. This theoretical work paves a new way towards electrochromic applications of CONASHs that harness the versatility of these materials.

5.2. STATEMENT OF CONTRIBUTION

This chapter includes one first-authored paper. The bibliographic details of the co-authored paper, including all authors, are:

Meng Li, Zhenzhen Wu, Hao Chen, Tim Gould, and Shanqing Zhang. First-principles exploration of two-dimensional benzenehexathiolate coordination nanosheets for broadband electrochromic devices. (Submitted to ***Advanced Functional Materials***)

My contribution to the paper involved:

The theoretical experimental design and implementation; the collection and analysis of data; the preparation of the manuscript.

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Name of Student: Meng Li

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Supervisor: Shanqing Zhang

5.3. ARTICLE 4

CHAPTER 6

BAND-STRUCTURE ENGINEERING OF COPPER BENZENEHEXATHIOL FOR REVERSIBLE MECHANOCHROMISM: A FIRST-PRINCIPLES STUDY

Submitted to Journal of Physical Chemistry C

6.1. INTRODUCTORY REMARKS

The findings and development in this chapter has been submitted to ***Journal of Physical Chemistry C***.

Many creatures can change their body colour based on their surroundings, such as cephalopods and chameleons. These abilities acquired during natural selection are controlled by movement of muscles and pigment-containing organelles, respectively. These mechanical action-induced chromism inspired researchers to invent artificial mechanochromic devices, which can change colours and optical properties under external mechanical stimuli. In this work, we theoretically discover mechanochromic effect in copper benzenehexathiol (Cu-BHT). The strain-induced changes in atomic charge, bond length and strength, and electronic structures are investigated in detail and correlated with critical mechanochromic properties. The related phenomena are based on band-structure engineering, providing Cu-BHT with ultrasensitive tunability in visible and near-infrared spectra under only 3% strain. Corresponding modulation ranges of transmitted energy are 2.7~74.6% and 0~87.6%, respectively, offering great potential in smart windows, thermal camouflage, infrared radiative cooling, and various nanoscale electronic and optoelectronic applications with multi-functions.

6.2. STATEMENT OF CONTRIBUTION

This chapter includes a co-authored paper. The bibliographic details of the co-authored paper, including all authors, are:

Meng Li, Zhenzhen Wu, Yuhui Tian, Feng Pan, Shanqing Zhang, and Tim Gould. Band-structure engineering of copper benzenehexathiol for reversible mechanochromism: A first-principles study for broadband electrochromic devices. (Submitted to ***Journal of Physical Chemistry C***)

My contribution to the paper involved:

The theoretical experimental design and implementation; the collection and analysis of data; and the preparation of the manuscript.

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Name of Student: Meng Li

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Corresponding author of paper: Shanqing Zhang

(Countersigned)_____(Date) 25/03/2022

Supervisor: Shanqing Zhang

6.3. ARTICLE 5

CHAPTER 7
CONCLUSIONS AND FUTURE WORKS

7.1 GENERAL CONCLUSIONS

We successfully discovered electrochromic and mechanochromic effects for smart windows in traditional inorganic materials and emerging CONASHs. This project provides further insights into the mechanism of corresponding phenomena and predicts electrochromic or mechanochromic performance as smart windows. The major findings from the works in this thesis can be concluded as follows:

1. The electrochromic effect of LTO came from the lithium intercalation-induced donor states, which gradually expanded and moved to the deeper levels in the forbidden band during lithiation, resulting in better conductivity and lower transmittance. The absorption of infrared light is highly sensitive to lithiation, in contrast to that of visible wavelengths. The modulation ranges of transmitted visible light, solar spectrum, and mid-infrared are 3.8-41.7%, 0.2-63%, and 0-70%, respectively, showing great potential in smart windows and infrared camouflage devices. This work suggests that introducing donor states can be used to modulate the absorption coefficient and electrochromic performance.
2. The structural stability of TiS_2 nanosheets was reduced with larger interlayer distances, resulting in more severely deformed and anisotropic Ti-S octahedrons in monolayer TiS_2. For bulk TiS_2, the bandgap between S-*p* and Ti-*d* increased by 0.05-0.11 eV during lithiation, while by 0.42-1.62 eV for monolayer TiS_2. The chemical bonding of Ti-S was substantially weakened, according to the COHP analysis (1.17-0.96 in bulk TiS_2, 0.64-1.15 in monolayer TiS_2). Lithium intercalation reduced absorption coefficient and reflection intensity, raising transmittance in solar spectrum with the modulation ranges for bulk and monolayer TiS_2 being 24-48% and 34-75%, respectively. This work suggests that for 2D nanosheets materials, their structural

stability, electronic and electrochromic properties are thickness-dependent, which could be utilized for modulating performance in electrochromic devices and more various applications.

3. TM-BHTs showed excellent structural stability that their lattice parameters changed no more than ±2.1% except -3.4% for Sc-BHT during lithium intercalation. The intercalation voltages generally increased with the atomic number of TM atoms. Among Mulliken charge of TM, S, and intercalation voltages, each pair had a good linear correlation ($R^2 \geq 0.90$), except for Co/Ni/Cu/Ag-BHT, due to the *d*-electron delocalization. The positive charge of Li came from the electron transfer to TM atoms, and the bond strength of Li-S and TM-S had an opposite relationship with the intercalation voltage, except for Pd/Ni/Cu/Ag-BHT. The Fermi levels located in the CB except for Mn/Mo/Ru-BHT with the band gaps less than 0.2 eV. As lithium insertion brought electrons filling in the *d* orbits of TM, Fermi levels were pushed to higher energies with increased electron conductivity of Mn/Mo/Ru-BHT and resistance of Cu/Ag-BHT, due to different DOS near the Fermi levels. In terms of electrochromic properties, Cr/Cu/Ag-BHT had the most obvious changes in colours. The adjustment ranges of transmittance for Cu/Ag-BHT were 68% and 41% in the visible region, 90% and 82% in the near-infrared region, respectively. For mid-infrared, the corresponding adjustment ranges of reflectivity are 84% and 74%, respectively. These excellent results indicate that Cu/Ag-BHT are promising materials for smart windows, thermal camouflage, and infrared radiative cooling devices, with superior optical and thermal management capabilities. This work clearly demonstrates the advantages of first-principles calculations for screening novel electrochromic materials.
4. For Cu-BHT, the biaxial strain of the same magnitude caused larger deformation and changes in bond strength than uniaxial strain. The asymmetric uniaxial strain had a

greater effect on the bond in the parallel direction than in the vertical direction, in terms of bond length and strength, as well as Mulliken charges of related atoms. These imbalances caused disproportionation phenomena in bond strength of S-Cu and Mulliken charge of S atoms, which could also be observed in ELF maps. The net change of Mulliken charge of total S atoms was neglectable, charge transfer was only between C and Cu atoms under external strain. The electronic structures were highly sensitive to external strain, with Fermi energies pushed to higher levels by compressive strain and lower levels by tensile strain, maintaining in the CB all the time. The former decreased DOS around Fermi levels and prolonged the band tail upwards, resulting in limited unoccupied states near the Fermi level. The latter was quite the contrary, leading to broken π-*d* conjugated system. Both strains negatively affected electron conductivity and interband transitions between S-*p* and Cu-*d*, resulting in lower absorption coefficient and higher transmittance. In terms of optical properties under strain, colour of transmitted visible light became brighter from dark violet of pristine Cu-BHT films. The excellent tunability of transmittance in the visible and near-infrared regions could be achieved under compressive strain in the range of 0-3%, with the corresponding modulation ranges being 2.7-74.6% and 0-87.6% for uniaxial and biaxial compressive strains, respectively. Moreover, transmitted energy in the visible and near-infrared regions could be separately regulated under biaxial compressive strain, due to different strain sensitivities, further saving energy in illumination and temperature control as smart windows. The ultrahigh reflectivity (91.2%), low transmittance, and high absorptivity of pristine Cu-BHT in mid-infrared offer great potential in the field of infrared camouflage systems and infrared radiative cooling devices, with tuning abilities in related functions. The prominent strain-tuneable electronic properties of Cu-BHT could also be utilized in the nanoscale electronic and optoelectronic applications.

The uniqueness of this work is to enrich the mechanism for mechanochromic smart windows.

7.2 FUTURE WORKS

This thesis has successfully discovered novel materials for electrochromic and mechanochromic smart windows with excellent performance via first-principles calculations. Corresponding mechanisms have been investigated in detail, which provides further insights into the phenomena of electrochromism and mechanochromism. However, besides these achieved progress, there are still more works that need to be performed in future studies:

1. For inorganic electrochromic materials like LTO, besides lithium intercalation, other methods (like higher-valence cation replacement, negative ion vacancies) which can introduce donor states in the forbidden band are predicted to cause the electrochromic phenomenon, which needs to be confirmed in more extensive research as well as their relationships with the electrochromic performance.
2. As TiS_2 nanosheets tend to deviate from the stoichiometric ratio with the insertion of titanium atoms in the van der Waals gap, the practical performance of TiS_2 nanosheets with various types of defects is worth more investigation.
3. The S atoms in TM-BHTs could be replaced by O, Se, and even -NH group, resulting in dozens of configurations. The electrochromic and mechanochromic effects in these compounds remain unexplored. Meanwhile, the laws of corresponding properties should be summarized to facilitate future screening processes.
4. Cu-BHT provides a novel mechanism for mechanochromic smart windows, which should not be an exception. More materials based on band-structure engineering should be discovered as well as more novel mechanisms for smart windows.