Title
Graphite Oxide Template Based Synthesis and Characterization of Metal Oxide Nanosheets

Permalink
https://escholarship.org/uc/item/52f1k6tp

Author
Tom, Kyle Brandon

Publication Date
2018

Peer reviewed|Thesis/dissertation
Graphite Oxide Template Based Synthesis and Characterization of Metal Oxide Nanosheets

By

Kyle B. Tom

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Engineering – Materials Science and Engineering

in the

Graduate Division

of the

University of the California, Berkeley

Committee in charge:

Professor Jie Yao, Chair
Professor Oscar D. Dubón
Professor Vivek Subramanian

Summer 2018
Abstract

Graphite Oxide Template Based Synthesis and Characterization of Metal Oxide Nanosheets

by

Kyle B. Tom

Doctor of Philosophy in

Engineering – Materials Science and Engineering

University of California, Berkeley

Professor Jie Yao, Chair

Two dimensional materials and their composite structures show unique and favorable properties for many different kinds of applications and physical studies. Isolated 2D materials have shown a unique array of physical phenomena, including the room temperature observation of the quantum Hall effect, as well as enhanced physical properties, including large exciton energies and extremely high carrier mobilities. Composites have shown enhanced performance in traditional applications, including enhanced photocatalysis and battery performance, that stems from a synergistic effect between the individual materials in the composite. However, there is a limited number of naturally layered materials, an even smaller subset that is stable in ambient conditions. As such, it is beneficial to find 2D materials with better properties that may originate from other types of crystals. It has been predicted certain types of crystal structures, such as wurtzite, will form a two-dimensional phase similar to αBN below a particular thickness threshold. ZnO, and its graphitic form (gZnO) is of particular interest due to its favorable optical properties and oxidation resistance. gZnO has also been shown to have superior piezoelectric performance over similarly structured most other 2D materials, including BN and transition metal dichalcogenides (TMDCs). It also has shown excellent properties for many other applications that range from magnetism to catalysis. However, forming such confined systems is difficult and has limited the lateral size significantly. This has limited experimental work on this system, prohibiting application and basic understanding.

This dissertation explores the use of a graphite oxide template technique that confines the growth direction to synthesize multiple metal oxide nanosheets, with specific focus on sub-nm ZnO. Graphite oxide, a chemically functionalized form of graphene, has many properties that are favorable for use as a template. The interlayer distance ranges from 0.6 – 1.2 nm, creating a nanosized reactor. Additionally, graphite oxide templates are hydrophilic; this allows templates to be easily synthesized in water by sonication and helps aqueous precursors be drawn in between layers. Because of these advantages, as well as the large template size and uniformity, graphite oxide offers a unique opportunity for nanosheet synthesis.

This method shows growth of nanosheets in the tens of microns size. The structure of these composites and the nanosheets are presented here, including TEM side view images of the stacking and fine geometry verification of the gZnO transition using XANES and thorough simulation
work. Changes in the optoelectronic properties are determined through various measurements including XAS, EELS, XPS, and electronic transport. In particular, gZnO has a massive increase in the bandgap and a strong enhancement in the Zn 4s state availability. Improvements and advantages of this method are shown, including the compatibility with plasma cleaning and doping.

In addition to van der Waals materials and thickness dependent structures, a significant amount of work has been focused on taking typical 3D crystals and growing them into two dimensions. This technique offered a way to synthesize some of these nanosheets. Fe$_2$O$_3$ was used as a test case and showed similar lateral sizes to the gZnO. Composites of the synthesized Fe$_2$O$_3$ nanosheets and the rGO showed strong interactions between the two, leading to some unique properties. The rGO transfers a significant amount of charge to the Fe$_2$O$_3$, most likely as a way to passivate the dangling bonds in the crystal. The XAS spectra of composites show significant formation of Fe$^{+2}$ like states, making the hematite appear more like magnetite or maghemite. The magnetic properties of Fe$_2$O$_3$ are measured using SQUID and XMCD. Composites show enhanced coercivity and saturation, but no change in the overall magnetic structure.

Other materials were also grown using this method, including doped and alloyed gZnO, NiO, and MgO. Various changes were observed, including strong changes in the core level shifts by XPS and the absence of an interlayer between SiO$_2$ and rGO. Some limits of this technique were also found, as Al$_2$O$_3$ and CuO showed distinct nanoparticle formation instead of nanosheet formation. Finally, a rule of thumb is presented for materials that are compatible with this technique in hopes that it can be further refined and used as a guide for future work in this direction.
To my parents, John and Denise, for fostering my curiosity and providing me with the opportunity to succeed, my brothers, Jason and Nathan, for their inspiration, and Florissa, for her unending patience, love and support.
# Contents

Contents ................................................................................................................................. ii  
List of Figures ............................................................................................................................. iv  
List of Tables ............................................................................................................................ vii  
List of Acronyms & Symbols ................................................................................................. viii  
Chapter 1 Introduction ............................................................................................................ 1  
  1.1 Motivation: 2D Nanostructuring for novel applications and enhanced 
    functionalities ......................................................................................................................... 1  
  1.2 Two dimensional materials .............................................................................................. 1  
  1.3 Two dimensional crystals of non-layered materials ....................................................... 5  
  1.4 Surface polarization and size dependent crystal structures ......................................... 6  
  1.5 2D composites and heterostructures ............................................................................. 10  
  1.6 Wurtzite ZnO .................................................................................................................. 13  
  1.7 Graphitic ZnO ................................................................................................................ 14  
  1.8 This dissertation ............................................................................................................. 17  
Chapter 2 Graphite oxide template growth of gZnO .............................................................. 18  
  2.1 Graphite oxide template method ................................................................................... 18  
  2.2 Optical and AFM imaging of gZnO nanosheets and composites ................................. 19  
  2.3 Crystallographic and morphological investigations of gZnO ....................................... 25  
    2.3.1 TEM investigation .................................................................................................... 25  
    2.3.2 GIWAXS measurements ......................................................................................... 31  
  2.4 Chapter 2.4: XANES and fine structure verification .................................................. 33  
  2.5 Optoelectronic properties of gZnO ................................................................................. 40  
    2.5.1 Electronic structure of gZnO ................................................................................... 40  
    2.5.2 Transport measurements ......................................................................................... 44  
  2.6 Alternative substrates and transfers .............................................................................. 46  
  2.7 High temperature annealing of gZnO ............................................................................ 49  
  2.8 Graphene oxide removal at lower temperature ............................................................ 52  
Chapter 3 Graphite oxide template synthesis of Fe₂O₃ nanosheets and composites .......... 55  
  3.1 Optical, AFM, and SEM imaging of Fe₂O₃ nanosheets .................................................. 56  
  3.2 Crystallographic Studies of Fe₂O₃ and Composites ...................................................... 58  
    3.2.1 Raman spectroscopy ............................................................................................... 58  
    3.2.2 TEM imaging ......................................................................................................... 59  
    3.2.3 GIWAXS measurements ....................................................................................... 60
List of Figures

Figure 1.1: Structures of various 2D materials and their electronic properties. ............... 2
Figure 1.2: Overview of 2D materials and their relative stability. ................................. 4
Figure 1.3: ZnSe nanosheets ....................................................................................... 6
Figure 1.4: Tasker classifications and example surfaces from common materials .......... 6
Figure 1.5: Schematic of electric field and potential in Tasker type 3 surfaces .............. 7
Figure 1.6: Surface terminations of semi-infinite ZnO slabs ....................................... 8
Figure 1.7: Comparison of the wurtzite and graphitic crystal structures .................... 9
Figure 1.8: Visualization of graphite oxide composite synthesis and morphology .......... 11
Figure 1.9: Hydrocarbon trapping and high quality interfaces ...................................... 12
Figure 1.10: Structure of wZnO and gZnO ................................................................. 14
Figure 1.11: Band structure comparison of wZnO and gZnO ........................................ 15
Figure 2.1: Schematic of graphite oxide template based synthesis .............................. 19
Figure 2.2: AFM of gZnO Nanosheets ................................................................. 20
Figure 2.3: A 18 um 3-layer ZnO nanosheet ............................................................ 21
Figure 2.4: Very large area gZnO sheet from collection of templates .......................... 21
Figure 2.5: Contrast of a monolayer ZnO nanosheet on a 300 nm SiO\textsubscript{2}/Si wafer. 23
Figure 2.6: TEM Imaging ......................................................................................... 25
Figure 2.7: HRTEM of thin “nanosheets.” ................................................................. 26
Figure 2.8: NBED Patterns of gZnO/rGO composite ............................................... 27
Figure 2.9: Side view imaging of gZnO/rGO composites ............................................ 28
Figure 2.10: HRSTEM image of a gZnO/rGO heterostructure ..................................... 30
Figure 2.11: GIWAXS Scatter plots of various ZnO samples .................................... 32
Figure 2.12: Radially integrated GIWAXS plots of various ZnO samples ................ 33
Figure 2.13: XAS of ZnO samples ................................................................. 34
Figure 2.14: XAS Spectra of a 4 layer gZnO structure .............................................. 35
Figure 2.15: rGO/ZnO composite XAS simulations .................................................... 36
Figure 2.16: 7 Layer wZnO in between graphene sheets ......................................... 37
Figure 2.17: XAS of 4-layer ZnO on SiO\textsubscript{2} ................................................ 38
Figure 2.18: XAS of gZnO covered by hydroxyl groups ........................................... 38
Figure 2.19: XAS of Bulk ZnO under tension ......................................................... 39
Figure 2.20: XAS results of gZnO with defects ....................................................... 40
Figure 2.21: X-Ray analysis of various ZnO samples .............................................. 41
Figure 2.22: Photoluminescence of ZnO nanosheets ............................................ 42
Figure 2.23: Calculated band offsets from X-Ray based analysis between gZnO and wZnO. 43
Figure 2.24: Low loss EELS of gZnO/rGO composite ........................................... 44
Figure 2.25: Electric tuning of sub-nm gZnO by ionic liquid gating ............................. 45
Figure 2.26: Composite grown on graphite ............................................................... 47
Figure 2.27: EDX Mapping of composite on graphene .............................................. 48
Figure 2.28: ZnO composite grown on a thin layer of Fe\textsubscript{2}O\textsubscript{3} ......................... 49
Figure 2.29: High temperature annealing of ZnO nanosheets ................................... 51
Figure 2.30: Side view image of a composite annealed at 700°C in vacuum .......... 52
Figure 2.31: RIE treatment of ZnO .......................................................................... 53
Figure 2.32: Side view image of Ar/O\textsubscript{2} plasma cleaned sample .......................... 54
Figure 3.1: Basic info on iron oxides with a focus on hematite. ........................................... 55
Figure 3.2: Fe$_2$O$_3$ Nanosheets and composites ............................................................... 57
Figure 3.3: Contrast of a Fe$_2$O$_3$ nanosheet on a SiO$_2$/Si wafer ..................................... 58
Figure 3.4: Raman of iron oxide samples .............................................................................. 58
Figure 3.5: TEM characterization of Fe$_2$O$_3$ composites ...................................................... 59
Figure 3.6: GIWAXS Scatter plots of various Fe$_2$O$_3$ samples ........................................... 61
Figure 3.7: GIWAXS investigation of strain in composites ..................................................... 62
Figure 3.8: Absorbance spectra of rGO and an rGO/Fe$_2$O$_3$ composite ............................. 63
Figure 3.9: XPS of various Fe$_2$O$_3$ samples ......................................................................... 64
Figure 3.10: XANES Spectra of bulk Fe$_2$O$_3$ and composite rGO/Fe$_2$O$_3$ ...................... 65
Figure 3.11: Magnetic SQUID measurements comparison between bulk Fe$_2$O$_3$ and a composite structure ................................................................. 66
Figure 3.12: XMCD comparison of Fe$_2$O$_3$ samples .......................................................... 67
Figure 4.1: AFM imaging of AZO nanosheets ..................................................................... 70
Figure 4.2: EDX dispersion of AZO ....................................................................................... 70
Figure 4.3: AZO XPS comparison of a 1% Al doped sample ................................................. 71
Figure 4.4: XPS measurements of Fe in Fe:ZnO samples ...................................................... 72
Figure 4.5: Fe:ZnO GIWAXS for different concentrations ..................................................... 72
Figure 4.6: XANES spectra of bulk Fe$_2$O$_3$ and Fe:ZnO composite structures with different Fe%. ................................................................. 74
Figure 4.7: AFM of a MgZnO nanosheet ............................................................................. 75
Figure 4.8: Side view image of a MgZnO composite ............................................................... 76
Figure 4.9: High Mg Concentration MgZnO nanosheet composite GIWAXS scan ............... 76
Figure 4.10: XANES of MgZnO nanosheets ....................................................................... 77
Figure 4.11: Rocksalt and CuO monoclinic crystal structures .............................................. 78
Figure 4.12: AFM images of a MgO nanosheet ................................................................... 79
Figure 4.13: TEM Characterization of MgO ....................................................................... 79
Figure 4.14: GIWAXS scatter plots of MgO samples ............................................................. 80
Figure 4.15: Radially integrated plots of the GIWAXS scatter plots for a MgO composite and bulk film ................................................................. 81
Figure 4.16: NiO Nanosheet AFM Images ............................................................................ 82
Figure 4.17: GIWAXS scans of NiO samples ..................................................................... 83
Figure 4.18: Radially integrated GIWAXS plots of NiO samples .......................................... 84
Figure 4.19: TEM investigation of NiO composites ............................................................... 84
Figure 4.20: Formation of Copper Oxide Nanoparticles ...................................................... 85
Figure 4.21: CuO nanoparticle formation within a composite structure ................................. 86
Figure A.1: Composite films after a “blow-off.” ................................................................. 91
Figure A.2: Using tape to peel off excess GO ................................................................. 92
Figure A.3: O$_2$ treatment comparison to normal drying conditions of GO ......................... 93
Figure A.4: Comparison of composite height vs nanosheet height .................................... 94
Figure A.5: NBED Diffraction images from “pure ZnO Nanosheets.” .................................. 95
Figure A.6: NBED Diffraction image from a multilayer composite structure ...................... 95
Figure A.7: Bulk wZnO First Excited state ......................................................................... 96
Figure A.8: gZnO First Excited State .................................................................................. 96
Figure A.9: XAS Simulation of 4 layer gZnO sandwiched between graphene sheets .......... 97
Figure A.10: XAS simulations of ZnO on SiO$_2$ covered by hydroxyls ............................. 97
Figure A.11: XANES simulations of other Zn containing compounds. ................................. 98
Figure A.12: GIWAXS data of all Fe$_2$O$_3$ samples .................................................................... 99
Figure A.13: Comparison of solution Al % versus measured Al% in solid samples. .... 100
Figure A.14: Comparison of solution Mg % versus measured Mg % in solid samples. 100
Figure A.15: Comparison of solution Fe % versus measured Fe % in Fe:ZnO solid samples. ........................................................................................................................................ 101
Figure A.16: Side view image of a intercalated GO sample ............................................................ 102
Figure A.17: Side view image and corresponding EDX scan of an Fe$_2$O$_3$ composite annealed in an Ar-96%/H$_2$-4% gas mixture for 1 hour at 600°C ................................................................................. 103
Figure A.18: AFM of an attempt at Alumina nanosheet synthesis .................................................. 104
Figure B.1: Schematic comparison of the two high resolution XAS techniques .......... 107
Figure B.2: Schematic of the decay of the XAS process for TEY .................................................. 107
Figure B.3: Schematic comparison of EXAFS and XANES ............................................................ 108
Figure B.4: Schematic of XMCD ................................................................................................... 110
Figure B.5: Schematic of the XMCD process and the resulting changes in the XAS spectra .................................................................................................................................................... 110
List of Tables

Table 1.1: Number of layers up to which the graphiticlike structure has a lower cleavage energy than the (1010) and (0001)/(0001) surfaces and the corresponding cleavage energies. 10
Table 1.2: A comparison of structural parameters between wurtzite and graphitic ZnO. 14
# List of Acronyms & Symbols

## Abbreviations:
- **AFM**: Atomic Force Microscopy
- **CBM**: Conduction Band Minimum
- **CL**: Cathodoluminescence
- **EBD**: Electron Beam Deposition
- **EBL**: Electron Beam Lithography
- **EDX**: Energy Dispersive X-ray Spectroscopy
- **EELS**: Electron Energy Loss Spectroscopy
- **EFM**: Electrostatic Force Microscopy
- **GIWAXS**: Grazing Incidence Wide Angle X-Ray Scattering
- **GO**: Graphene Oxide
- **rGO**: Reduced Graphene Oxide
- **gZnO**: Graphitic ZnO
- **wZnO**: Wurtzite ZnO
- **HAADF**: High Angle Annular Dark Field
- **FIB**: Focused Ion Beam
- **IL**: Ionic Liquid
- **ILG**: Ionic Liquid Gating
- **NBED**: Nanobeam Electron Diffraction
- **PL**: Photoluminescence
- **RIE**: Reactive Ion Etching
- **RS**: Rocksalt Phase
- **SEM**: Scanning Electron Microscopy
- **SPM**: Scanning Probe Microscopy
- **SQUID**: Superconducting Quantum Interference Device
- **STEM**: Scanning Transmission Electron Microscopy
- **SXRD**: Surface X-Ray Diffraction
- **TEM**: Transmission Electron Microscopy
- **TEY**: Total Electron Yield
- **VBM**: Valence Band Maximum
- **XANES**: X-ray Absorption Near Edge Spectroscopy
- **XAS**: X-ray Absorption Spectroscopy
- **XMCD**: Xray Magnetic Circular Dichroism
- **XPS**: Xray Photoelectron Spectroscopy

## Symbols:
- \( E_A \): Electron affinity
- \( E_b \): Binding energy (XPS)
- \( E_{\text{vac}} \): Vacuum energy level
- \( E_{\text{BS}} \): Electrostatic energy between planes
- \( E_{\text{OP}} \): Electrostatic energy between oppositely charged planes
- \( I \): Intensity
- \( \Phi \): Phase change due to changes in the optical path
\( r_i \)  Effective refractive index
\( C \)  Gate capacitance
\( q \)  Charge of an electron
\( \mu_e \)  Electron mobility
\( V_{SD} \)  Source-drain voltage
\( V_G \)  Gate voltage
\( V_{th} \)  Threshold voltage
\( I_{SD} \)  Source-drain current
\( n_e \)  Electron concentration
\( g_m \)  Transconductance
\( \sigma \)  Surface charge
\( \text{Oh} \)  Octahedral site
\( \text{Td} \)  Tetrahedral site
\( V \)  Potential
\( V_{\text{Total}} \)  Total potential in the crystal
\( \mu \)  Absorption coefficient
\( E \)  Energy
\( P \)  Density
\( Z \)  Atomic number
\( A \)  Atomic Mass
Acknowledgements

It is imperative I thank the many people who have helped me throughout the process of writing this dissertation. It would be not be an exaggeration to say that without them, this would not have been possible.

First, I must thank my advisor, Professor Jie Yao, for taking a risk on working with me as his first student.

I would also like to acknowledge Professor Oscar Dubon for being a wonderful mentor from my early days as an undergraduate and still providing me with support with my dissertation and for general advice. It is no small statement to say I would not be where I am currently without him.

I would like to acknowledge Professor Daryl Chrzan for help on my Master’s thesis and Professor Vivek Subramanian for his help in preparation of this dissertation.

I must also thank all of his group members, both great colleagues and friends. I want to thank Shuai Lou, Yang Deng, Shuren Lin, Yin Liu, Zilun Gong, Fuyi Yang, Rui Chen, Qingjun Wang, Xi Wang, Nolan Ahlm and Sujung Kim.

I am also extremely grateful to my many collaborators inside and outside the university. David Prendergast and Liwei Lin from the Theory of Nanostructures group who were gracious enough to work much longer on the simulations than intended, and provided the critical evidence for the gZnO as well as an immense amount of other insight. Alpha N’Diaye for taking his own time to help obtain the critical XAS data and help me piece together our initial ideas. Karen Bustillo, Song Chen, and Burak Ozdol for providing all of the support for the TEM and FIB. Karen went above and beyond her job at NCEM, helping me obtain the data I needed. I also want to acknowledge Jie Wang and Dafei Jin for their help with side view images and Junwei Huang and Hongtao Yuan for their work on the electronic transportation. I also want to acknowledge Shancheng Yan and Hui Wu for their contributions to the project.

This work was primarily supported by the Laboratory Directed Research and Development Program of Lawrence Berkeley National Laboratory under U.S. Department of Energy Contract No. DE-AC02-05CH11231, as well DOE contracts with the Advanced Light Source and Molecular Foundry.

I want to also thank my friends and family: my parents, John and Denise, for encouraging me to follow my dreams of pursuing a career in science and my brothers, Nathan and Jason, for their emotional support and inspiration.

Finally, I want to acknowledge my fiancée and partner for more than 10 years, Florissa. She has provided emotional support, encouragement, and humor through this monumentally difficult time. She has shown incredible patience for my late nights and weekends, for my frustrated attitudes, and for a general 5 years of ups and downs. She was critical for my success, and I am extremely grateful.
Chapter 1  Introduction

1.1 Motivation: 2D Nanostructuring for novel applications and enhanced functionalities

Inspired by the initial work on graphene, intense focus has been given to increasing the family of 2D nanomaterials in search for new engineering opportunities and physics that may help enhance technologies in energy, optoelectronics, and catalysis as well as increase our understanding of natural phenomena. 2D materials are the atomically thin form of van der Waals or layered materials that have strong in plane bonding and weak van der Waals bonding between planes. The weak out of plane bonding allows the sheets to remain, relatively, chemically stable and can be easily isolated mechanically without damaging the structure of the monolayer. The formation of 2D sheets has a myriad of benefits, including ultrahigh specific surface area and strong confinement of charge carriers in a two-dimensional plane, both of which can enhance interactions in chemical processes and optical processes for applications in energy storage, solid state lighting, and photocatalysis. These applications are critical for developing next generation technologies that will help address growing technical demands.

For studying 2D materials, the most common way to create nanosheets is by isolating single or few layers of a layered crystal, such as MoS$_2$ or BN. However, this limits the 2D studies to only a select group of materials. An enormous amount of work has gone into fabricating 2D structures out of non-layered materials with 3D atomic bonding. This would allow every material to have a 2D counterpart, allowing the various advantages in the 3D case to be used or enhanced in the 2D form. An optimistic view also expects unique properties and enhanced functionality.$^1$ Indeed, many reports have shown enhanced performance as a result of nanosheet structuring, even when used in a pressed or stacked form. Despite significant promise, many challenges remain, primarily regarding synthesis. It is difficult to control the lateral size, thickness, and crystal phase at the atomic scale using chemical synthesis. Additionally, exfoliation is not a favorable option due to the lack of the van der Waals bonding in the bulk crystal.

This dissertation aims to provide additional options and understanding to these stated disadvantages, through use of a unique system, both as a template and as a base material. Specifically, a unique form of ZnO that forms a planar structure below a certain threshold may alleviate some of the non-uniformity by making atomically flat planes preferable. Additionally, utilizing 2D materials as a template can utilize the ease of fabrication that 2D materials enjoy to ease the synthesis of other nanomaterials.

1.2 Two dimensional materials

The field of two dimensional materials began many years before the discovery of graphene. Monolayers of materials have been grown either by epitaxy or other thin film methods for many years.$^2$ However, it was not until graphene was isolated that the field grew rapidly. Several factors were important for graphene. First, the method for obtaining it was incredibly cheap and easy. Mechanical exfoliation by scotch tape$^3$ with a graphite crystal is a very low barrier to research. Second, the material could be isolated onto almost any substrate, making it possible to be used for many applications and studied with a large number of techniques. Third, it could be easily found on top of a Si/SiO$_2$ substrate, and could easily be verified as monolayer through AFM and Raman spectroscopy. Since the discovery of exfoliated monolayer graphene, there have been an incredible
number of studies performed on van der Waals layered crystals, such as BN and MoS$_2$, at the nanoscale. The number of layered materials is finite, but it is ever growing with increasingly exotic materials. As seen Figure 1.1, 2D material bandgaps and active optical regions span from deep UV to radiowaves, with a wide variety of band alignments. It has grown to include materials that exhibit ferromagnetism$^{4,5}$, superconductivity$^6$, and phenomena more unique to 2D systems specifically, such as the room temperature observation of the quantum Hall effect$^7$. 

**Figure 1.1: Structures of various 2D materials and their electronic properties.** a) Schematic showing the energy range over which the 2D materials field covers and includes several structural examples. b) Electronic band structures of four common 2D materials and their bandgap energies. c) Band energy alignments of many 2D materials with favorable optoelectronic properties in the visible range. Adapted from$^8$. 

Graphene deserves special mention as it has incredibly unique properties and has enabled a wealth of new physics. However, before mentioning any of those, it is worthwhile to discuss some of its outstanding properties. Graphene has a Dirac cone dispersion with no gap$^9$ which enables some fantastic electronic properties, including a carrier mobility of up to 10000 cm$^2$V$^{-1}$s$^{-1}$ at room temperature$^3$, ambipolar charge transport, and the ability to tune the carrier concentration easily through electric field effect$^{10}$. Single layer graphene only absorbs 2.3% of light,$^{11}$ effectively making it transparent. However, this absorption quickly becomes very significant as the number of layers increases. Suspended graphene nanosheets demonstrate incredibly high thermal conductivities, up to 5000 Wm$^{-1}$K$^{-1}$$^{12}$. Single nanosheets show incredibly high mechanical strength, with a Young’s modulus of 1 TPa.$^{13}$ This strength also comes with significant flexibility due to the atomically thin size. Graphene has a specific area, defined as the amount of surface area...
per unit mass, of 2633 m$^2$/g, making it incredibly useful for surface area dependent applications that include catalysis and adsorption. These exceptional properties are sought for all kinds of applications and massive amounts of research has and will be performed to bring this material to market. These core properties drive a significant amount of the research dedicated to utilizing graphene for various applications, including next generation electronics and energy storage.

A particularly useful derivative of graphene is its oxidized form, graphene oxide (GO), as this material has been researched as an easy way of fabricating monolayer graphene. Typically, graphite oxide is first made using the Hummers method, or a similar method. Graphite is mixed with sodium nitrate, and sulfuric acid at ~66°C before cooling to 0°C. Potassium permanganate is added to the solution and mixed. After, water is added. The solids are filtered out and cleaned with phosphorus pentoxide. The leftover solid is graphite oxide, a layered material similar to graphite except with functional groups replacing some carbon atoms. Typically hydroxyl, epoxy, and carbonyl groups are the main attachments. The C/O ratio depends on the exact method, but often varies between 4:1 and 2:1. These functional groups have several consequences which will be discussed below. An unfortunate side effect of these functional groups is the dramatic reduction of the conductivity of the sheets. However, reduction methods can be used to bring GO sheets close to pristine graphene. The simplest method is through heating in an inert atmosphere. Typically, the higher the temperature, the more reduced the graphite oxide. For example, changing the heating temperature from 500°C to 750°C changed the C/O ratio from around 7 to above 13, which corresponds to a conductivity change from 50 S/cm to 100 S/cm. Annealing up to 1100°C allowed the conductivities to reach 550 S/cm. Annealing in reducing atmospheres, such as hydrogen or ammonia, can lower the temperature necessary to reach high conductivities, as well as bind residual oxygen from imperfect vacuum systems. Although chemical methods exist for reducing graphite oxide or graphene oxide, this work will focus on high temperature options due to its usefulness for the synthesis technique introduced later.

As mentioned previously, other than for producing graphene sheets easily at large scale, graphite oxide has many unique properties created by the functional groups. First, the functional groups allow graphite oxide to be hydrophilic, which causes its interlayer spacing to expand and fill with water when submerged. In this way, different chemical species can be intercalated between the layers. Immersion in water also creates significant negative charge, creating an electrostatic repulsion, allowing the graphene oxide to remain dispersed in solution. Additionally, these functional groups can act as preferential nucleation sites or adsorbent sites. The most common use for these graphene oxide sheets and the functional groups is as a platform to graft different molecules and materials. For example, grafting isocyanates allows the graphene oxide sheets to be dispersed in polymers and add electrical conductivity. More importantly, these reactive oxygen functional groups of GO enable researchers to conduct further chemical functionalizations to render GO an ideal platform for the accommodation of adsorbents such as biomolecules, which is a key factor for its bio-related applications.

As seen from graphene and GO, 2D materials hold many exciting properties and engineering benefits. However, many of these materials, especially the more exotic combinations, suffer from major stability issues. A good example is black phosphorus, a layered material with strong anisotropic behavior and a buckled layer structure. A monolayer of black phosphorus will survive in normal ambient conditions for anywhere from 20 min to 1 hour before complete degradation. Typically, this is due to water and oxygen in the atmosphere. While this is an extreme case, many materials are unstable in ambient for long periods of time, and even fewer at elevated temperatures. Even BN, a highly stable material at high temperatures in air, will begin to
oxidize around 700°C for high quality samples. Figure 1.2 summarizes groups of known materials and their relative stabilities.

The stability of 2D materials can be summarized for a few sensible rules of thumb. 1) 3D materials with high melting points (over 1000°C) have the best chance for having a stable 2D configuration. 2) The 3D parents must be chemically inert in the environment and must not have a surface that decomposes or reacts. In most cases, this will be ambient conditions, so oxidation by air or water vapor becomes the most likely reaction. The surface requirement is particularly important, as many materials are stable due to the formation of a passivation layer which prevents further reactions, such as Al₂O₃ on aluminum or SiO₂ on Si. These layers are typically only nanometers in thickness. However, 2D nanosheets are essentially surface only, so any reaction with the surface would cause a complete reaction in the 2D nanosheet. 3) Insulators and semiconductors tend to be more stable than metallic 2D materials as they are less reactive. Verification is typically fairly straightforward, usually by Raman, AFM, or optical microscopy, although in plane conduction or out of plane tunneling are more definitive.

![Figure 1.2: Overview of 2D materials and their relative stability. Blue means stable in ambient. Green are most likely stable, although there may be some stoichiometric changes. Gray means materials that have been exfoliated down to monolayer, but little else is known. Pink indicates materials that are unstable in atmosphere at low layer numbers, but may be stable when encapsulated or in inert atmospheres. Figure adapted from.](image)

On top of this, great effort has been placed into stabilizing these materials, typically by encapsulation by impermeable materials, whether it be an organic attachment or other more stable 2D materials such as graphene. Exfoliation in an inert atmosphere followed by encapsulation by another material, usually BN, or exfoliation in solution (NMP/ethanol) have both been successful in stabilizing 2D materials that would otherwise degrade. However, this can still greatly reduce the usability (for example, nanosheets in solution cannot be used for electronic applications) and greatly complicates utilization as mechanical stacking is a relatively time-consuming process and generally adds defects. Additionally, these encapsulation materials or solvents can alter the properties of the vulnerable material. Despite this, the 2D materials community has flourished because of the many favorable and interesting properties, such as thickness property tuning, enhanced exciton behavior, and the reduction of surface states.
1.3 Two dimensional crystals of non-layered materials

In addition to typical layered materials, many studies have focused on bringing conventional 3D crystals to the 2D realm, such as ZnSe nanosheets seen in Figure 1.3. The large surface-to-volume ratio is an attractive property for many applications, including catalysis and gas sensing. They have also been used in a large variety of applications, including as supercapacitors, photocatalysis, chemical sensing, and battery electrodes. Additionally, these materials could expand the parameter space of 2D materials and add some additional benefits, including enhanced harsh condition stability, chemical/biological compatibility, and a wider range of band alignments for electronic devices. There are a variety of ways to grow these materials. Some rely on a template to do a solution-based epitaxy process. This is the case for gold on top of graphite. Others rely on ligands to preferentially attach to certain crystal faces of the material, forcing the growth in certain directions. Others rely on a material transformation, usually by an oxidation process. One example is the growth of Fe₂O₃ nanosheets. First, FeOOH is synthesized, which is a layered material, and chemically exfoliated using an ultrasonic cleaner to obtain FeOOH nanosheets. These can be annealed in air to obtain 1 µm wide half nanometer thick Fe₂O₃. All of these processes have some disadvantages, including reproduction and large-scale uniformity. Many of these materials still have not reached thicknesses close to 1 nm, and their later sizes tend to be a few microns or smaller. As such, a new growth method is preferred that can be used with a variety of materials, in addition to providing high levels of reproducibility and uniformity. Few, if any, of these materials are able to form true monolayers, as they are still limited by their natural crystal structures. Additionally, due to the existence of dangling bonds, many of the non-oxide and some non-stoichiometric oxides materials degrade quickly, usually as a result of oxidation, and need surfactants to protect them. A new crystal system that can utilize the 2D advantages without being explicitly 2D may provide the best opportunities for integration.

Metal oxides are particularly useful for a variety of reasons. Metal oxides tend to have strong stability for photocatalysis and water splitting, mostly due to its resistance to further oxidation relative to non-oxides. This is especially important for nanomaterials, since even a single layer of unwanted oxidation can cause massive changes. Additionally, they have favorable band gaps for UV applications and good insulating properties for applications such as supercapacitors. Metal oxide surfaces are also quite active, which is great for battery electrodes and photocatalysis. Some oxides are currently available, but may suffer from stoichiometry changes (TiO₂) or are toxic (V₂O₅, MoO₃), and may still be unstable due to being in not the fully oxidized phase. As such, new nanosheets of nonlayered oxides may provide plenty of engineering opportunities, especially since nanostructuring has been found to drastically alter the properties, both as a result of a hierarchial structure and due to the shape and size effects.
1.4 Surface polarization and size dependent crystal structures

In parallel with these studies, it has recently been shown that certain types of materials will undergo structural changes when their thicknesses reach below a particular threshold. This transformation is caused by the instability of polar surfaces. As a brief overview, there are three types of surfaces in ionic crystals classified by Tasker, as shown in Figure 1.4. A type 1 surface is neutral, in which the number of positive and negative ions cancel each other out so that each plane has no net charge. This can easily be seen along the {100} rocksalt planes, in which there are the same number of positive and negative ions with the same magnitude of charge in each layer. A type 2 surface is charged. In this configuration, each plane has a net charge. However, due to the symmetry of the ions, all dipole moments cancel, such that the total dipole moment in the crystal is negated. This is the case for anatase (TiO$_2$) {110} planes. A type 3 surface occurs when alternating planes of opposite charge introduce a finite dipole moment in the crystal, such that the total electrostatic energy diverges with increasing crystal size, as is the case for wurtzite ZnO {0001} planes.

![Figure 1.3: ZnSe nanosheets a) Structure of ZnSe. Notice there is no van der Waals bonding, and significant bonding contributions in all three dimensions. b) TEM image of nanosheets.(500nm, 100nm). c) AFM image of ZnSe nanosheets (500 nm). Images adapted from.](image)

![Figure 1.4: Tasker classifications and example surfaces from common materials. Red arrows indicate the direction of the dipole moments. Figure adapted from.](image)
Figure 1.5: Schematic of electric field and potential in Tasker type 3 surfaces. a) Uncompensated. b) Compensated. Dotted lines correspond to the continuous potential profile, while the continuous lines indicate the alternating electric field magnitude.

Figure 1.5 demonstrates this divergence in detail. Each plane is assigned a surface charge, ±σ. As such, each set of two planes acts as a parallel plate capacitor, with potential

\[ V = 4\pi\sigma R_1 \] (1.1)

Where \( R_1 \) is the distance between the positive and negatively charged planes. For a crystal with \( N \) sets of oppositely charged planes, the total potential becomes

\[ V_{total} = 4\pi N\sigma R_1 \] (1.2)

And the total electrostatic energy becomes

\[ E_{total} = 2\pi N\sigma^2 R_1 \] (1.3)

For a typical bulk crystal, \( N \) approaches infinity and \( E_{total} \) also approaches infinity. As this is thermodynamically very unstable, there often needs to be a charge compensation mechanism to prevent the divergence. Generally speaking, this involves a change in the surface charge only. Essentially, the surface charge magnitude is reduced to \( \sigma' \) which is equal to

\[ \sigma' = \frac{\sigma R_2}{R_1 + R_2} \] (1.4)
This changes the magnitude of the electric field such that it is finite between sets of oppositely charged planes. The electric field between the oppositely charged planes is

$$E_{OP} = \frac{4\pi \sigma R_2}{R_1 + R_2} \quad (1.5)$$

And the electric field between sets of planes is

$$E_{BS} = \frac{4\pi \sigma R_1}{R_1 + R_2} \quad (1.6)$$

The potentials cancel each other out, such that effectively the potential oscillates between a finite value and 0. At the very top surface of the crystal, the potential is not compensated, so there is a small finite residual energy, such that the total potential is

$$V'_{Total} = \frac{4\pi \sigma R_1 R_2}{R_1 + R_2} \quad (1.7)$$

However, it does not diverge and is negligibly small over crystals of just a few layers or larger.

![Figure 1.6: Surface terminations of semi-infinite ZnO slabs. A) STM image of triangular islands on a Zn terminated surface. b), c), and d) are potential different configurations of the islands. e) A side view schematic of the (White – Zn, Dark – O. f) STM image of an O-terminated surface. Figures adapted from references 48,49](image)

The way the surface charge is altered can occur through many different mechanisms. For materials exposed to atmosphere, it is very common for species to adsorb on the surface. For instance, hydrogen will generally introduce positive charges while hydroxyls will generally introduce negative charge on a surface, which can act as a way to partially compensate the charge. Water, which can dissociate into hydroxyl groups on highly reactive surfaces, and hydrogen are nearly ubiquitous in atmosphere, and very difficult to remove from even specialized vacuum chamber. They have been found to change the surfaces of structures under high vacuum, showing how difficult it is to study pristine surfaces and how much of an impact hydrogen and water can have on the surface structures of materials. However, for other systems, it is more common for a top surface to have incomplete layers. Using ZnO as an example, Zn has an $R_1$ of roughly 0.61-0.63 Å and an $R_2$ of 1.95-1.99 Å, giving a $R_1/(R_1+R_2)$ factor of around $\frac{1}{4}$. Figure 1.6 shows the Zn terminated (0001) surface of ZnO that forms half-unit-cell tall, or one Zn-O layer, triangular islands on top of the crystal.\textsuperscript{48,49} These islands have an outer edge consisting only of O. These
triangles generally form a size in which ¼ of the Zn atoms are missing from the surface, reducing the overall surface charge. For the O terminated surface, hexagonal terraces form, and the charge is primarily compensated by hydrogen. Another method which often takes place in addition to the surface reconstruction methods described previously is surface relaxation. Essentially, the top layer of ions will move closer to the bulk of the crystal. This reduces $R_1$ and causes a similar change to changing the surface charge. In the case of ZnO, the Zn layer shrinks down into the O layer slightly, and both layers move closer to the next set of planes.\(^5\) These two mechanisms can also work together. For example, the Zn terminated configuration is also calculated to have a 7% relaxation.\(^5\)

![Figure 1.7: Comparison of the wurtzite and graphitic crystal structures.](image)

For ultrathin crystals, another mechanism is available in which the crystal undergoes a complete structural change. Typically, the oppositely charged planes converge into a single plane, which eliminates the dipole moment and effectively changes the surface from a type 3 tasker surface to a stable type 1 tasker surface that has no net charge in each plane and no electric field in the crystal. Reference \(^{45}\) predicted that the wurtzite family of materials, which includes GaN, BeO, SiC, ZnS, and ZnO, will undergo a transition from a wurtzite structure, that has a buckled anion and cation layer, to a graphitic layer with a structure very similar to BN (Figure 1.7). Although the structure is closer to BN, especially with the 2-element composition, most literature refers to these materials as graphitic, such as graphitic ZnO or gZnO. Table 1.1 displays the theoretically predicted number of layers under which the transformation of the graphitic phase occurs. Of the materials studied, BeO has highest thickness threshold at 30 layers, while the lowest threshold belongs to ZnS and SiC at around 4 layers. This is quite a large variation, and stems from the chemical nature of the constituent atoms, specifically whether or not the constituent atoms are likely to form sp\(^2\) hybridization. C, N, and O can easily form threefold planar configurations, but S and other 2\(^{nd}\) row elements, with relatively weaker multiple bonds, prefers tetrahedral coordination. The second consideration is from electronic structure. Graphitic structures are insulating, unlike the metallized surfaces of their bulk counterparts. The metallization occurs as a result of charge transfer, so if the charge is unable to transfer, the graphitic phase will persist. As such, a larger electronegativity difference and a larger band gap create a stronger preference for the graphitic phase. This means a larger electronegativity difference actually helps this transformation. Considering these materials adopt a planar structure with sp\(^2\) hybridization that is usually a signature of strong covalent bonding, this is a relatively surprising result. It is worth noting that the wurtzite structures do not form a graphitic structure in the monolayer case under all
conditions. Additionally, in some models, the top layer of ZnO shows a relaxation, such that the structure is in between $gZnO$ and $wZnO$.

The only widely accepted family of materials that is expected to undergo this transformation is the wurtzite crystal family (Figure 1.7). These materials are expected to have very different properties when compared with their bulk phase and may serve to link true 3D and true 2D structures. There has been some theoretical work for the rocksalt structure, although the energy between a normal configuration and a graphitic-like structure are minimal, making it difficult to synthesize.

Table 1.1: Number of layers up to which the graphitic structure has a lower cleavage energy than the $(10\overline{1}0)$ and $(0001)/(000\overline{1})$ surfaces and the corresponding cleavage energies. Adapted from45.

<table>
<thead>
<tr>
<th>Film</th>
<th>number of layers</th>
<th>graphitic $\rightarrow (10\overline{1}0)$ cleavage energy (J m$^{-2}$)</th>
<th>number of layers</th>
<th>graphitic $\rightarrow (0001)/(000\overline{1})$ cleavage energy (J m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>12</td>
<td>3.9</td>
<td>24</td>
<td>6.5</td>
</tr>
<tr>
<td>BeO</td>
<td>8</td>
<td>2.3</td>
<td>30</td>
<td>8.6</td>
</tr>
<tr>
<td>GaN</td>
<td>6</td>
<td>2.9</td>
<td>12</td>
<td>5.5</td>
</tr>
<tr>
<td>SiC</td>
<td>4</td>
<td>3.5</td>
<td>8</td>
<td>7.7</td>
</tr>
<tr>
<td>ZnO</td>
<td>10</td>
<td>2.0</td>
<td>18</td>
<td>3.5</td>
</tr>
<tr>
<td>ZnS</td>
<td>4</td>
<td>1.4</td>
<td>10</td>
<td>5.2</td>
</tr>
</tbody>
</table>

GaN and ZnO are of particular interest due to their favorable properties in such fields as UV optics and sensing. ZnO has the additional benefit of strong resistance to oxidation, and it is compatible with the synthesis technique I will introduce later.

### 1.5 2D composites and heterostructures

The development of graphite oxide allowed the simple synthesis of graphene oxide nanosheets dispersed in water and aqueous environments. This opens up a cheap, fast, and low-cost way to create graphene-like composites (Figure 1.8). Typically, the composite structures look to combine some functional nanomaterial with graphene in order to utilize advantages from both of the materials while minimizing disadvantages from each. For example, graphene oxide composites hope to utilize one of its unique properties mentioned above, which have been extended and listed below:

1) Provide a highly conductive pathway for less conductive materials.
2) High surface area/surface-to-volume ratio in order to utilize more active sites.
3) Ultrathin thickness that shortens the diffusion distance of ions for applications in lithium ion batteries.
4) Structural flexibility and strength for flexible applications and improved durability.
5) Thermal and chemical stability.
6) Abundant surface functional groups for grafting functional groups and for hydrophilicity.
7) Due to its band structure, a broad electrochemical window that increases the maximum energy density.

On the other hand, the second component material tends to add functionality that is not found in graphene, or at least has a superior property relative to standard graphene. Metal oxides can be added to improve the UV absorption and add semiconducting behavior for applications like...
photocatalysis. Magnetic nanoparticles can be added in order to make the composites magnetic or superparamagnetic for biomedical applications. Dielectric materials can be added in order to create supercapacitors. Pd has been added to create materials for gas sensing. Many other applications have been demonstrated, and readers are pointed to references in.

As with any good advancement in a field, the sum of the two materials are greater than its parts. In other words, there are advantages to composite structures that are not visible in either material. For example, both nanomaterials and GO, without the use of surfactants, tend to agglomerate in solution over time. By mixing two materials together, the individual GO sheets and nanoparticles stay separated such that they utilize their individual behavior. Additionally, as is the case in lithium ion batteries, the composite structure suppresses the volume change of metal oxide nanoparticles, increasing the cycling stability of the electrode. There are also simple synergistic improvements in properties, such as the higher specific capacity of Fe$_2$O$_3$/rGO composites compared to Fe$_2$O$_3$ or rGO only.

There is one additional reason why composites are particularly promising in the near future compared to graphene itself. It is incredibly difficult to synthesize pristine, single crystal graphene over large areas or roughly wafer scale. Polycrystalline graphene performs much worse than pristine graphene, and residues left behind by transfer processes can alter many fundamental properties. However, composites do not require large areas of graphene, typically only a few microns are necessary. This is easily achievable by common exfoliation techniques, such as sonication in a solvent.

These materials are generally synthesized in one of three ways. One is to take premade graphene oxide and nanomaterials and mix them together in a solvent. This is the easiest to control the ratios of the materials and there are no changes to the individual synthesis. However, it is difficult to control the dispersion of nanomaterials. The next is to combine graphite oxide and a nanomaterial system and then reduce both at the same time. This method typically relies on nucleation sites at GO defects to create a more uniform dispersion. The last is one pot synthesis in which graphene oxide is fabricated in the same solution as the nanomaterial or nanomaterial precursor. This is often the simplest method but is more difficult to control and is less understood due to multiple processes occurring at once. There are other methods to fabricate these materials, but generally they fall under one of these categories or a combination of two. This dissertation will
focus on a combination of the last two methods, creating the GO and mixing it with the precursor solution, then reducing GO and oxidizing the precursor.

Figure 1.9: Hydrocarbon trapping and high-quality interfaces. a) Low magnification STEM image of a graphene-BN-graphene-BN structure on top of SiO$_2$. b) HRSTEM image of the structure in the boxed area. The top graphene layer has been removed due to contamination, but the BN and bottom graphene layer form an atomically sharp interface. c) Electrical properties of the top (red) and bottom (black) graphene layer. Adapted from 60.

A more ordered, and generally much thinner, analogue to these composites is vertical heterostructures (Figure 1.9). Heterostructures, which can be considered a few-layer composite of two or more different monolayers stacked on top of each other, have also attracted an immense amount of attention, primarily due to the rich physics that dominate these systems. Typically, heterostructures can be utilized to produce new phenomenon not observed in monolayer systems. One of the earliest examples is graphene on BN, which drastically improved the mobility of carriers in graphene,\textsuperscript{61} which enabled the observation of Hofstadter’s butterfly and the fractal quantum hall effect.\textsuperscript{62} Incorporating other materials such as MoS$_2$ and WS$_2$ adds effects that originate from band gaps and excitons, including the observation of interlayer excitons.\textsuperscript{63} Many unique phenomena and applications have been discovered in this highly exciting field, but the scope is too broad to cover here and the reader is guided towards some excellent reviews.\textsuperscript{34}
Additionally, there are also lateral heterostructures which have received considerable attention, but are difficult to synthesize and share very little similarities to the structures I synthesized.

One important detail, however, is the fabrication of these heterostructures. Generally, heterostructures are made by mechanically transferring one material on top of another material that is already on a substrate. This often traps contamination between the layers, typically hydrocarbons and water (Figure 1.9). While this normally does not adversely prevent the realization of many phenomena, it can cause issues when trying to approach high performance applications. Additionally, it is very time consuming to perform the transfer, and can be tricky to consistently perform the transfer. The second major method is by growing the heterostructures together using methods such as CVD or PLD. This method is difficult to perform, requiring very carefully tailored conditions. In this way, easy heterostructure fabrication is still an ongoing effort.

1.6 Wurtzite ZnO

Zinc oxide has been widely studied, as it has favorable properties in fields ranging from food additives to catalysis. As mentioned previously, it preferentially forms the wurtzite crystal structure (wZnO, Figure 1.10a), a hexagonal system in which each atom is tetrahedrally coordinated. Zincblende and rocksalt ZnO have also been observed, but usually requires special considerations, such as high pressures (RS) or substrate interactions (ZB). Typically, ZnO grows preferentially along the (0001) planes, which gives strong texturing behavior when performed on a substrate. This crystal structure also lacks inversion symmetry, allowing it to exhibit piezoelectricity and pyroelectricity. It has a wide, direct bandgap ($E_G = 3.3$ eV) and a relatively high mobility, making it useful for applications such as UV absorbers, efficient light emitters, and transparent conductors.

ZnO is typically intrinsically n-type doped. This is caused by the formation of native defects that act as donors. The exact defect that acts as a donor is still under hot debate, and the most recent and most convincing argument is for a hydrogen atom that occupies an oxygen vacancy. Nevertheless, it is widely agreed that the carrier concentration, and the conductivity, can be modified by inducing oxygen vacancies, typically through processing or post annealing in vacuum. Unfortunately, ZnO’s preference for n-type doping makes it very difficult to dope it p-type. Even after decades of study, p-type ZnO has not been reliably demonstrated. Conventional doping methods have failed, while more exotic options have limited reproducibility and produce dubious results. The main reason cited for the difficulty in p-type doping ZnO is compensation, where defects will form to offset the p-type doping or dopants will form compounds that no longer act as acceptors. This has ultimately prevented ZnO from attaining industry status, where SiC and GaN are the preferred materials. Despite this, research on ZnO systems is still quite active. Most importantly, however, is the formation of a Tasker 3 surface, which allows it to form the graphitic phase.
### 1.7 Graphitic ZnO

Figure 1.10: Structure of wZnO and gZnO. Structure models of a) wZnO and b) gZnO. Structure factor intensity of the c) 10l, d) 11l, and e) 20l surface diffraction rods. f) The corresponding structure determined by the structure factor intensities. c-f) adapted from 66.

Table 1.2: A comparison of structural parameters between wurtzite and graphitic ZnO. Adapted from 66.

<table>
<thead>
<tr>
<th></th>
<th>wZnO</th>
<th>gZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter, (a/c)</td>
<td>3.25/5.2</td>
<td>3.3/4.9</td>
</tr>
<tr>
<td>U parameter, Å</td>
<td>0.63</td>
<td>0</td>
</tr>
<tr>
<td>(d_{Zn-O}) in plane, Å</td>
<td>1.95</td>
<td>1.92</td>
</tr>
<tr>
<td>(d_{Zn-O}) out of plane, Å</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>Bond Angle</td>
<td>109.25</td>
<td>120</td>
</tr>
<tr>
<td>Coordination</td>
<td>4</td>
<td>3/5</td>
</tr>
</tbody>
</table>

The first experimental realization of gZnO after the theoretical prediction was in 2007 by Tusche et al., 66 shown in Figure 1.10. They utilized thermal evaporation of Zn on Ag, followed by a cycle of oxidation. This formed islands of two layer and greater ZnO. Through rigorous surface X-ray diffraction (SXRD) or grazing incidence XRD (GIXD), they were able to determine the nature of the stacking as well as the important structural parameters. They also found that the thickness needs to be below 1 nm to form gZnO, a much stricter requirement than theoretically predicted and a significant cause for the difficulties in synthesis. Since then, the phase has been fabricated on additional metal substrates, 67, 68 in a metastable nanocrystalline form with surfactant stabilization (although with unusual lattice parameters), 69 and in graphene nanopores. 70 The major structural differences between wZnO and gZnO are listed in Table 1.2. The in-plane lattice parameter expands 1.6% from 3.25 to 3.303 Å, and the interlayer spacing is approximately 2.45
Å. The Zn-O bond distance also shrinks from 1.95 Å to 1.92 Å. Due to strong covalent and ionic bonding, the coordination number can be considered 3 or 5, although 3 is more valid for the monolayer.

gZnO has many interesting properties and advantages over other 2D materials. First, gZnO does not suffer from oxidation. Zn only forms with a Zn 2+ charge, so it is very resistant to oxidation or reduction even at higher temperatures. As previously mentioned, this is very different from many 2D materials, which will often oxidize or be damaged at high temperatures in ambient, including graphene and BN. Some, as previously mentioned, are unstable even at room temperature. There is some concern with interactions with H causing instability, however the concentrations used can be relatively high.

Monolayer gZnO was calculated to have a specific area of 2836 m²/g. This is slightly higher than that of graphene. BN is also expected to have a similar specific area due to a very similar bonding length and weight. While ZnO has a higher weight per 6 atom ring, almost double, it also has an increased bonding length that gives almost double the area for this ring. In addition, due to its stronger ionicity, it may be more likely to interact with various chemicals. Although conversely, this may point to lower stability of the gZnO when compared to graphene. Simply looking at the bulk ZnO material proves this point. ZnO is amphoteric, meaning it will dissolve in both acids and bases that graphene will not, including NaOH, a chemical used heavily in graphene transfer from Si/SiO₂ substrates.

Due to the difficulty of synthesizing and isolating gZnO, most studies have been relegated to simulations. Initially, many studies calculated the bandgap of 2D gZnO to be only slightly larger than the normal ZnO bandgap of 3.3 eV. This is counterintuitive, as quantum confinement alone would cause a very large increase. A more refined approach found a much more nominal increase, up to 5 eV. This bandgap appears much more reasonable, especially after work done with two-layer GaN, which demonstrates a 4.8-5 eV bandgap regardless of crystal structure. These values are also smaller than the bandgap of monolayer BN (~6 eV), the most similar material to gZnO, and is larger than common metal chalcogenides. This means gZnO fits well in between BN and other conventional 2D materials. Almost all simulations have pointed to a direct bandgap for ZnO at the Γ point (Figure 1.11), making it useful for many optoelectronic applications. Additionally, the conduction bands were found to be primarily created from Zn 4s and O 2p states for both gZnO and wZnO. This is understandable, as the structural changes are not so significant to drastically alter the electronic properties.

Figure 1.11: Band structure comparison of wZnO and gZnO. Band structure of a) wZnO, b) bulk gZnO, and c) monolayer gZnO. In c) the gray area indicates the band gap after GW₀ corrections. Images altered from reference 74.
Highly ionic crystals, such as ZnO and other wurtzite materials, can be advantageous for electromechanical applications. Interestingly, ZnO is one of the few materials that can exhibit piezoelectricity in bulk and in its 2D phase. All multi-element 2D materials are piezoelectric, as they lack an inversion symmetry. However, bulk wZnO also lacks inversion symmetry. The only form of ZnO that could not have piezoelectricity is 2-layer ZnO, as it still has inversion symmetry. From simulations, it was found that gZnO is more flexible than graphene and has stronger piezoelectric behavior than BN ($d_{11, gZnO} = 0.48e/Å$ vs $0.23e/Å$). In fact, gZnO surpasses most 2D materials. Of similarly structured planar 2D nanomaterials, such as graphene or BN, it has the highest. This combination of flexibility and large piezoelectric coefficient is advantageous for piezoelectric applications. It is difficult to compare the strength of wurtzite to graphitic ZnO due to a different polarization direction and the overall different matrix scheme due to reduced dimensionality and a different structure, but it can be considered similar.

In fact, there is an incredible amount of simulated results for many different kinds of functionalization and applications. One heavily pushed aspect from reference 78, determined that gZnO could act as a very good substrate for graphene. This is due to the mismatch and low interactivity between the gZnO and graphene. Essentially, Van der Waals forces indicate a very low interaction initially. On top of that, gZnO and graphene have such a large difference in their in-plane lattice spacing that the charged Zn and O ions do not interact with the C atoms in graphene. There is very little charge transfer, indicating the graphene can retain its high mobility, and a very small gap opening, ~ 5 meV, even with defects, such as oxygen vacancies or Al and Li doping, indicating that this is a robust phenomenon that can be realized in experimental systems. However, this heterostructure system induces a charge redistribution in the graphene plane in which intra-layer electron-hole puddles form. These puddles massively increase the carrier concentration. Since gZnO was highly anticipated for optoelectronic properties, they also looked at the optical properties of gZnO, graphene, and gZnO/Graphene heterostructures and showed that there is enhanced absorption in the UV and visible regions. However, this result may be a bit suspect due to an unusually low simulated bandgap for monolayer ZnO.

Significant effort has been made in identifying interesting dopants. Most metallic dopants, including Al and most transition metals, show a low barrier for Zinc substitution (~tens or hundreds of meV) and thermodynamic stability. Most, however, prefer an adsorption configuration. A few, such as Mn, show some preferential adsorption in the center of the ZnO heterostructure. However, most preferentially attach above O atoms where the large electronegativity difference creates a significant charge transfer. Ren et al. did an exhaustive study looking at how transition metal doping affects the electronic and magnetic properties of gZnO, and showed that Mn, Fe, Co, Cu, and Ni are all able to induce magnetism, opening the gateway for two dimensional dilute magnetic semiconductors (DMSC) potentially at room temperature. B, C, and N doping can cause similar effects, but experimental realization is much more difficult. Nitrogen in particular has been vexing, as it has been studied as an option for creating p-type ZnO. However, many barriers remain, including difficulties in retaining atomic N instead of N$_2$ and a much more difficult process than typically used for n type dopants such as Al. As in wZnO, N is also predicted to p-type dope gZnO. It remains to be seen if N can be incorporated more successfully in gZnO. A study on aluminum doping shows n-type behavior as well as CO oxidation.

Other interesting studies have been done on hydrogen storage, thermoelectricity, and nanoribbon metallicity, research that deserves significant attention, but is outside the scope of this document. As can be seen from the above information, there are a lot of intriguing aspects of
gZnO and some useful properties for engineering of 2D systems. It is therefore imperative to obtain experimental data, to both confirm theoretical predictions and to provide a realistic platform for study.

Despite such promise, facile synthesis gZnO remains elusive. All of the current synthesis techniques are extremely cumbersome, requiring high vacuum and specialized growth conditions. In addition, they are restricted to either very small sample sizes or to a specialized metal substrate. Many techniques that have been used are also unable to reach the sub-nm threshold at all. All of these disadvantages make it difficult to use the gZnO for any practical purpose, or even study many of its properties. In addition, free standing ZnO is important in order to understand the intrinsic properties of this unique phase, in addition to being essential for certain applications. Transfer also remains difficult, as ZnO is easily etched by both acidic and basic solutions.

1.8 This dissertation

The remainder of this document is as follows: Chapter 2 describes the method used to synthesize our gZnO samples and their properties. Chapter 3 will discuss hematite iron oxide (α-Fe₂O₃) nanosheet synthesis using the same technique and study its intrinsic and composite properties. Chapter 4 will discuss the synthesis of other materials and their properties and will include a discussion about the general guidelines for compatibility of this technique.
Chapter 2  Graphite oxide template growth of gZnO

While the gZnO phase may have many advantages, it is currently unknown how this phase transformation from wZnO will change the properties of ZnO due to the difficulty of synthesis and characterization. As an alternative to conventional chemical or physical deposition methods, template-based synthesis, utilizing nanosized gaps, has been shown to create nanostructures of ZnO and other materials with well-controlled morphologies; this provides inspiration for forming 2D sheets in a comparable way.\textsuperscript{85,86} Recently, GO has been used as a template for the synthesis of films and small, thick sheets of metal oxides through the intercalation of aqueous precursors.\textsuperscript{87} Due to the confinement of the GO during the formation of ZnO and naturally large lateral size of GO sheets, it is expected that this method, with some alterations, can be utilized to form sub-nm nanosheets that are much larger than those fabricated previously. This study has two important implications. The first is that this is a model system for characterizing materials undergoing thickness dependent structural changes. This system will elucidate how these types of changes can affect the properties of other materials that will have a similar thickness dependent structure, particularly those of the wurtzite crystal family. The second is that by studying the structure and other properties of alloyed and intrinsic ultrathin ZnO, it may be possible to understand stable configurations of other 3D crystals in new 2D layered phases.

Section 2.1 will describe the graphite oxide template process and the purpose of choosing graphene oxide as the template. Section 2.2 will show optical and AFM images of these sheets. Section 2.3 will be dedicated to crystallography studies using of composite structures and attempts at forming freestanding sheets, as well as discussions on the morphology of composites using TEM and GIWAXS. Section 2.4 presents X-Ray absorption near edge spectroscopy studies (XANES), including simulations, of nanosheets and composite structures to determine the fine structure of the zinc oxide nanosheets and confirm the planarity of the structure. Section 2.5 will present optoelectronic studies of gZnO. Section 2.6 discusses the importance of the substrate and potential opportunities for transfer. Chapter 2.7 explores the effects of higher temperature processing of the nanosheets. Section 2.8 discusses potential for low temperature removal of graphene oxide. It should also be noted that most of the information in this chapter originates from my and my colleagues\textsuperscript{88} manuscript.

2.1 Graphite oxide template method

Graphite oxide was chosen as the template to synthesize gZnO for several reasons. First, it is easy to create large and extremely thin samples through simple sonication in water. This allows the formation of large gZnO sheets. Second, these sheets are normally very uniform, resulting in similarly uniform thickness gZnO nanosheets. Third, graphite oxide is hydrophilic, which helps facilitate the incorporation of the aqueous precursor. It also has a relatively large interlayer spacing (~0.8 nm) that expands in water, which allows the precursors to intercalate. Finally, graphite oxide is able to provide oxygen to the precursor in order to form ZnO. Due to the textured growth of ZnO, the 0001 direction will be blocked by the graphene, inhibiting growth on its surface and forcing lateral growth. Zinc acetate dihydrate (Zn(O\textsubscript{2}CCH\textsubscript{3})\textsubscript{2}⋅(H\textsubscript{2}O)\textsubscript{2}) was used as a precursor material as it dissolves sufficiently in water and it has a preference for forming crystals with an 002 orientation.\textsuperscript{89}

The growth outline is shown in Figure 2.1. The growth procedure starts with sonicating GO powder in water for at least 15 minutes at a ratio of 3 mg/mL, or down to 0.03 mg/mL for
studying individual sheets. Longer times increase the number of thin sheets but shrinks the lateral size of the sheets. Alternatively, commercially available graphene oxide solutions can also be used. The sheets are then dropcasted and dried on a substrate using a hotplate, then placed in an aqueous solution of 10 wt% Zn acetate dihydrate for at least 8 hours. Once again, due to the hydrophilicity, the GO will expand, and the capillary force will cause intercalation of the precursors in between the gaps. After sufficient time has passed, the samples are rinsed in DI water and dried in vacuum at 80°C for roughly an hour. The samples are then baked at 500°C in Ar with a ramp rate of 5°C/ min, in order to induce crystallization while being confined by the GO template while the GO reduces to reduced graphene oxide (rGO), providing an oxidative environment, and then is cooled down naturally. The slow ramp rate can prevent gas buildup which can lead to bubble formation and breakage, although this can be used advantageously. This forms a rGO/gZnO composite. Finally, the GO is removed by calcination in air at 600°C or higher with a ramp rate of 5°C/ min.

2.2 Optical and AFM imaging of gZnO nanosheets and composites

Atomic force microscopy (AFM) gives angstrom level thickness resolution. This is the most common method of measuring monolayer heights of 2D materials, and also works well for surface roughness studies for thin films. Also, it does not require a conductive substrate, unlike STM, and can be performed in various conditions, including ambient environment. This makes it very versatile and easy to use. Figure 2.2a and b show an SEM and an AFM image, respectively, of a monolayer ZnO sample on a Si wafer at the end of synthesis showing excellent uniformity. The linescan, Figure 2.2c, shows a measured thickness of about 2.8 Å, which is within the range of measured monolayer heights seen in literature. This value may be slightly larger than the true value due to the tapping mode AFM offsets and effects from a different substrate as is the case for graphene. Figure 2.2d and e show an optical image of the rGO/ZnO composite after the Ar bake and of the ZnO after the air bake, respectively. After burning in air, thicker areas of the sample are still visible, however thinner parts (below 2 nm in thickness) become invisible in an optical microscope. This is quite different from other 2D materials and can be explained by differences in the refractive indices, as will be discussed below. Figure 2.2f shows an AFM image of the boxed area in Figure 2.2e, showing that the ZnO nanosheets possess a layered structure well
defined by the ZnO/rGO template seen in Figure 2.2e. This indicates that the sheets form due to the intercalation of the zinc precursor in between GO sheets, and that thicker templates will create thicker ZnO sheets. Comparison of the composite and nanosheet thicknesses are shown in Figure A.4. Figure 2.2g shows the step-like profile of the line scan along the dashed line in Figure 2.2f. From the linescan, the thickness of the thin piece (1st step) is about 5.3 Å, which corresponds closely to the thickness of bilayer gZnO (the interlayer distance is about 2.4 Å). The AFM image also clearly shows a second bilayer, which shows a very clear indication of a flat, layered structure of gZnO sheets.

Figure 2.2: AFM of gZnO Nanosheets. a) SEM image of a monolayer gZnO nanosheet on Si (scalebar 1 µm). b) AFM image of the monolayer nanosheet (scale bar 1 µm). c) Corresponding linescan of the white line in b). Optical image of the d) ZnO/rGO composite and e) ZnO nanosheets (scale bar 3 µm). Yellow lines indicate the outline of the composite shown in d). f) AFM image of the dashed box area in d) and e) (scale bar 3 µm). g) corresponding linescan of the white line in f).
Figure 2.3: A 18 um 3-layer ZnO nanosheet. a) SEM and b) AFM topographical image of an approximately 18 µm nanosheet (Scalebar 50 µm and 5µm respectively). c) Linescan along the white line in b).

Figure 2.4: Very large area gZnO sheet from collection of templates. a) SEM and b) AFM topographical image of an nanosheet made from a collective of templates that is over 50 µm in one axis. The AFM image is rotated 180° relative to the SEM image. c) Linescan along the white line in b).
There has been no observed limit to the size of these gZnO samples. From a single template, samples up to 20 µm have been observed. Figure 2.3 shows SEM and AFM images of a 3-layer gZnO sheet after the burning of the GO, with a corresponding linescan. The size is roughly 20 µm across, and the thickness is about 0.8 nm, which roughly corresponds to a trilayer gZnO sample. However, even larger samples have been observed. Figure 2.4 shows an SEM image of a nanosheet, and an AFM image of a portion of the SEM image. As can be seen, the SEM image shows the length to be upwards of 50 µm, and the AFM shows that the portion we measured was approximately two layers. This is from a sample in which there were a film of one to three layers covering the surface. It appears that the films are thin enough of a template, and form such a continuous film on the surface, that the gZnO can still form as a single sheet. GO samples covering the surface. It appears that the films are thin enough of a template, and form such a continuous film on the surface, that the gZnO can still form as a single sheet. There are some areas where it varies from 1-3 layers or greater but is still impressive for such a large sheet. This provides an enormous potential for forming very large area gZnO for various studies. For a perfectly blown off film, the size of the gZnO can reach chip scale, as can be seen in Figure A.1. This should be taken with caution, as it is very difficult to measure the AFM over such a large area. Additionally, thicker pieces can be mixed in still, the concentration is just much lower and the space between them tends to be much greater than 100 µm or more. This allows these samples to be measured using much larger beamsize, such as XAS and X-ray Photoelectron Spectroscopy (XPS). Additionally, the high percentage of sub-nm samples indicates that an arbitrary beamsize could be used, although there appears to be some limitations as given by the GIWAXS results shown later. In fact, this prospect became very intriguing to reproduce if it could be controlled. Details on these films are discussed in Appendix A1.

It was originally expected that sub-nm ZnO should still be visible, similar to how monolayer graphene and BN are still visible on SiO2/Si substrates due to interference and contrast. This originates from the relative refractive indices of SiO2 and ZnO. ZnO has a refractive index much closer to SiO2 (1.47 at 400 nm) than either BN (2.2 across visible spectrum 91) or graphene (2.6 - 1.3i at 400 nm) at visible wavelengths. Reference 92 derives the equations for contrast using a 3-layer system: Si, SiO2, and the nanosheet material. Using normal incidence and assuming a semi-infinite Si slab, the equation for the intensity of the light can be described by equation

\[ I(n_1) = \left| r_1 e^{i(\Phi_1 + \Phi_2)} + r_2 e^{-i(\Phi_1 - \Phi_2)} + r_3 e^{-i(\Phi_1 + \Phi_2)} + r_1 r_2 r_3 e^{i(\Phi_1 - \Phi_2)} \right| \times \left( e^{i(\Phi_1 + \Phi_2)} + r_1 r_2 e^{-i(\Phi_1 - \Phi_2)} + r_1 r_3 e^{-i(\Phi_1 + \Phi_2)} + r_2 r_3 e^{i(\Phi_1 - \Phi_2)} \right)^{-1} \]  \tag{2.1}

\[ r_1 = \frac{n_0 - n_1}{n_0 + n_1} \]  \tag{2.2}
\[ r_2 = \frac{n_1 + n_2}{n_1 - n_2} \]  \tag{2.3}
\[ r_3 = \frac{n_2 + n_3}{n_2 - n_3} \]  \tag{2.4}
\[ \Phi_j = \frac{2\pi n_j d_j}{\lambda} \]  \tag{2.5}

Where \( \Phi \) is the phase shift due to the changes in the optical path and \( r_j \) are the relative indices of refraction. In order for the nanosheet to be visible, the intensity of the reflected light from the 3-layer system must differ from the light off of the silicon substrate without the nanosheet. This contrast can be defined as
\[ C = \frac{I(n_1 = 1) - I(n_1)}{I(n_1 = 1)} \quad (2.6) \]

In previous systems, the bulk refractive indices are used due to the index being mostly due to in plane interactions with normal incident light. In our case, although there is a structural change, for these calculations, I assume the overall change does not drastically alter the optical properties in the visible region, which some theoretical results agree with.\(^7\) In the calculations, Si has the largest change with wavelength, given by \(^9\). The refractive index of air is approximated as 1. \(\text{wZnO}\) has a refractive index of about \(n = 1.68\) to 1.55 across the visible range.\(^9\) The imaginary part is near 0 between at visible wavelengths above 400 nm, reaching a maximum value of 0.02i at a peak near 615 nm. Figure 2.5 shows the contrast of \(\text{ZnO}\) on 300 nm of \(\text{SiO}_2\) on Si, using the maximum value refractive index and assuming the imaginary part is 0 as it is negligibly small. Over the visible region, the \(\text{ZnO}\) contrast just barely surpasses 1%, which is much weaker than other similar 2D materials. For reference, single wavelength contrast values for graphene and BN can reach up to 12% and 4%, respectively. Additionally, the positive and negative contrast over the visible region means a decreased sum of contrast in white light conditions.

\[ \text{Figure 2.5: Contrast of a monolayer \text{ZnO} nanosheet on a 300 nm \text{SiO}_2/\text{Si} wafer.} \]

The thickness of the nanosheets have been confirmed to be below 1 nm in thickness, implying the formation of \(\text{gZnO}\). As such, a more direct method to prove structural changes is necessary. Initially, Raman measurements were performed in order to determine if there was a structural change. Since Raman measurements are related to the vibrational modes of a material, changes in the structure often are reflected in the Raman spectra. However, Raman spectra showed no peaks, and measurements on composites only showed contributions from rGO. One reason for the absence of Raman spectroscopy is the large bandgap of \(\text{gZnO}\). Graphene and similar 2D materials rely on resonance Raman to have a very strong spectra for such a thin material. Essentially, Raman spectral features are enhanced when the energies are near or above an electronic transition. The lasers commonly used for Raman, 633-450 nm, is far below the bandgap energy of \(\text{gZnO}\) and therefore cannot produce strong Raman signal. This is not absolutely necessary, as BN has a large bandgap but is able to produce some Raman features even in the monolayer case. However, BN nanosheets are single crystalline. As I will discuss later, the \(\text{gZnO}\)
I produce is polycrystalline. This means phonon and vibrational modes are scattered at grain boundaries and as a result, are much weaker than for single crystalline sheets.

Currently, there are three top candidates for proving the phase: Grazing incidence x-ray diffraction (GIXD), side view TEM, and x-ray absorption spectroscopy (XAS).

GIXD was the technique used for originally proving the existence of the gZnO phase. GIXD is similar to typical x-ray diffraction (XRD), except the incident beam is at a very small angle (<2°). This limits the depth of probing to approximately the first 10 nm, reducing signal from the substrate. This is key for measuring ultrathin films. It has a high enough resolution to determine the in-plane lattice parameter. Structure factor analysis would also give additional information on the stacking but requires a very uniform and crystalline samples over a very large area, something that is difficult to obtain with this method.

Another option is to create a side view image of our material. Essentially, a protective layer would be deposited on top of a sub-nm sample or composite, and a focused ion beam (FIB) would be used to mill out a section of the substrate and the sample. This would create a side view image which would be able to image the Zn and O. This would allow the distance between them to be measured. Since the Zn-O vertical distance changes from 0.63 to 0 Å, a high quality TEM would have the capability to resolve this change. This is a very promising method as it is a very direct measurement and the analysis is very straightforward. Plan view is omitted as an option, as the in-plane lattice parameter change is too small to resolve in TEM imaging and other methods require large, single-crystalline areas that do not exist for my samples.

The last promising option is XAS. Using synchrotron radiation, the x-ray absorption coefficient as a function of the x-ray photon energy of the material is measured near an absorption edge of a particular element. Due to interference effects from scattered photoelectrons, the measured absorption coefficient will have fluctuations with frequencies depending on the nearest neighbor element and distance. This technique can reach a resolution down to 0.02Å, which can resolve the small changes in the bonding distance of the ZnO. The pre-edge features and edge-shape also indicate changes in coordination, local geometry, and oxidation number. Additionally, it is good for dilute systems and surfaces due to its high sensitivity, making it a great choice for my samples.

All three options will be discussed below after the crystalline verification is discussed.
2.3 Crystallographic and morphological investigations of gZnO

2.3.1 TEM investigation

Figure 2.6 TEM Imaging of bulk ZnO. a) STEM, b) diffraction pattern, and c) TEM-EDX of a typical sample grown on a Ni grid with a holey SiO$_2$ membrane. Scale bar in a) is 40 nm.

The first step was to determine the crystallinity of pure sheets. For transmission electron microscopy (TEM) characterization, growth of the nanosheets were performed directly on holey SiO$_2$ TEM grids. Diffraction was performed initially on the thick, porous nanosheets (Figure 2.6). Porosity is very common for sol-gel like processes, however, there is a secondary reason that will be introduced later. The diffraction shows clear polycrystalline rings the index well to the expected rings of ZnO. Interestingly, the ZnO shows reflections from the 0002 direction, which is unusual given that the ZnO is normally strongly textured along the 0002 direction and should not be visible in the plan view of these samples. It is clear that the temperatures and process are sufficient for producing ZnO crystals. As a side note, occasionally small amounts of unburned GO were found attached to these crystals. These are most likely heavily damaged from the high T and were not completely burned away. This typically only occurs for very thick samples, as it requires a lot more time and energy to completely burn away large amounts of C, especially if they are trapped between ZnO sheets. Thinner sheets, usually determined by the initial template size observed through STEM contrast, are more unusual. Samples from thinner templates appear to completely decompose away, only appearing in small (~500 nm) size flakes near the edge of the hole (Figure 2.7). They also appear to not be porous, another unusual departure from the bulk case. Under STEM conditions, these flakes broke down within a few seconds, even at 60 kV. Due to the small size, normal diffraction was not possible. Instead NBED, nanobeam electron diffraction, was used to determine if there was any crystallinity. NBED uses a probe beam a few nm in size to probe very small areas for crystallinity. It also allows different areas to be scanned with the probe such that the probe is only on a particular area for a few seconds, helping to prevent some of the damage to the samples. From NBED diffraction, diffraction patterns were obtained that correspond well to ZnO (Figure A.5). However, like in the bulk case, various peaks were obtained that did not agree with gZnO and strongly textured ZnO. This pointed to the formation of larger ZnO particles that had grown without the texturing. However, some diffraction included the 1010 peaks, the normal peaks expected for textured ZnO. The lack of 6-fold symmetry from these peaks is most likely due
to tilt, since these overhanging samples often had large folds and a large amount of tilt, especially under the probe. However, this shows that thinner samples retain the crystallinity. This method could not provide sufficient quality data or thickness information for these samples, so it is unknow if these are gZnO. The crystallinity was not always perfectly consistent over the sheet, although this is difficult to determine due to the damaging of the samples. The samples did show crystallinity at various points within the sheet. Near the edge of the circle was where a majority of the crystallinity was found, which is logical given the more stable support it would have there. More details were found from HRTEM imaging.

![HRTEM image](image)

Figure 2.7: HRTEM of thin “nanosheets.” a) Low magnification STEM image of a “nanosheet” after calcination. b) HRTEM image of a “nanosheet” showing multiple few-nm crystalline regions with the correct 10\(\overline{1}0\) lattice spacing.

From HRTEM images (Figure 2.7), both crystalline and amorphous areas are observable in thinner samples. Typically, only lattice fringes are seen, not the hexagonal symmetry. This is most likely due to tilt, as in the NBED patterns from before. As in the two cases above, the majority of the sample shown appears to be amorphous, with some crystalline regions a few nanometers in size mixed in. This is consistent with our local diffraction probing technique which shows that crystallinity can generally be found anywhere but is localized near the edges where I believe it is more stable.

From the images, we are getting suspended crystallinity. However, the full samples we show in HRTEM images have a large percentage of amorphous areas. This will be discussed further below.

I also wanted to confirm that zinc oxide crystallizes in the composite form, and that there is sufficient energy to reduce the GO and oxidize the Zn. This is critical, as this will confirm that gZnO layers can be synthesized within the composite and without a substrate. HRTEM can provide Moire patterns between the GO and ZnO lattices, but diffraction provides more contrast and easier verification. Interestingly, normal diffraction through the composite only shows the diffraction from the GO. This is most likely due to the high quality of the GO diffracting most of the electrons. Additionally, the polycrystalline nature of the ZnO means the intensity of the ZnO is spread over a ring instead of 6 points, making its overall intensity much lower. NBED was used instead to see if the electrons could be focused through a single ZnO grain. The beam is approximately 2 nm at
the conditions used, which is small enough for a single gZnO grain. An example diffraction pattern is shown in Figure 2.8. The ZnO intensity is much weaker still compared to the GO, but it is still clearly visible. In Figure 2.8, a powder diffraction ring is shown inside a single crystal hexagonal pattern from the GO, due to the smaller spacing of GO planes, with only diffraction from the [0002] zone axis visible. The lower intensity may point to reduced crystal quality or, more likely given results from FIB samples seen later, a smaller amount of ZnO compared to GO. This shows that the sheets are indeed crystalline in the composite, and that the ZnO crystals are growing in between the sheets of GO. Additionally, because the GO confines the ZnO, the diffraction is most likely from sub-nm ZnO sheets. The powder diffraction pattern of the ZnO confirms that it does not align with the GO in any particular way and indicates that the GO does not strongly interact with the ZnO. The d spacing of the ZnO was determined to be around 2.85±0.08 Å, which corresponds closer to the spacing of the {1010} gZnO (2.86 Å) versus wZnO (2.81 Å). Figure A.6 also shows that ZnO forms between layers of multiple sheets of GO, showing that growth can happen between misaligned sheets.

There are a few other interesting observations from NBED measurements. It is difficult to consistently find diffraction in thin samples. This is most likely due to the lack of filling. Additionally, this technique, much like our HRTEM before, cannot prove the gZnO. One, it is difficult to obtain thickness information. Secondly, the resolution of the diffraction is not good enough to differentiate between such a small in plane change.

As mentioned previously, the large amorphous regions in the pure nanosheets are very unusual. After confirming the crystallinity in composite structures, there are two leading options.

First, the amorphous areas are ZnO. I find this fairly unlikely due to the fact that we see so much crystallinity in other areas. Additionally, literature results show ZnO will almost always crystallize near 400°C. At high temperatures, it is unlikely the amorphous film would not convert to wurtzite or graphitic. Additionally, data seen later from the XANES structure shows signatures more reminiscent of a planar transition than an amorphous film, although this is not definitive in
any particular way. I am also able to observe crystallinity in the composite from diffraction measurements, which is processed at a lower temperature than the final products. Although these are not confirmed to be sub-nm samples, the conditions are correct.

The second possibility is that there is some residual carbon that has not completely burned away. From our experiments, this would be odd as we do not normally observe it in AFM, etc. However, the fact the samples of unburned carbon are only on the order of 50-100 nm, it would be very easy to miss. The incomplete burn-off may also be due to the presence of the carbon membrane or another factor we may not have considered. In this situation, gZnO samples would sit on top of partially unburned carbon, which can appear amorphous, allowing the gZnO to be suspended and observable. Side view images, seen below, appear to support this analysis.

However, there are a few other complications. First, the nanosheets are visibly curved. This means a relatively small area would be aligned well to see lattice spacings. The second is the existence of carbon contamination. It has been shown in other 2D materials systems that carbon contamination can make it nearly impossible to reliably image the crystalline structure over large areas. While furnace cleaning can help in our case, exposure to ambient and handling often leads to the reformation of carbon contamination.

The best way to test this would be EDX, however, these samples crumble extremely easily and so getting reliable signal is difficult. This is in addition to almost ubiquitous carbon contamination which makes it even more difficult to interpret. At the very least, studying side view images of the composite can give a preliminary look at some of the unusual observations.

Figure 2.9: Side view imaging of gZnO/rGO composites. a) Large field-of-view image of the composite showing a bulk crystal forming inside of a wrinkle of rGO and a uniform interface layer. b) HRSTEM image and corresponding EDX and intensity maps of a side view composite sample.

Side view images were obtained by using FIB to cut a thin lamella from a composite structure on a Si chip. There are many different interesting features seen in the lamella of the composite, as seen in Figure 2.9. First is the large bulk crystal that has formed. This is most likely caused by wrinkles in the composite that form naturally during dropcasting. This can be seen in a smaller degree in other areas where the thicknesses are larger than 1 nm. This is difficult to control.
in very thick composites, as particles and irregular stacking preferentially create wrinkles and voids. However, thin sheets typically will have much fewer wrinkles overall, such that it is not a critical factor in the processing. The second is the very obvious bright sub-nm features found throughout the composite. These are ZnO sheets, easily visible due to Z contrast in STEM mode. This shows that ZnO sheets with the appropriate thickness can be formed in only the composite, likely creating a composite of gZnO and GO. However, a very important detail emerges. Within the composite, the sub-nm features are restricted to typically 2-10 nm lengths. This is drastically different from what we observe in our AFM samples, which have reached sizes upwards of 50 µm. However, this is most likely explained by the last interesting feature in the image. Right at the interface between the silicon and the composite is a bright, nearly atomically flat, complete, and incredibly long feature that corresponds to a very large ZnO sheet. Although impossible to view over large distances, the same feature can be seen spanning the entirety of the lamella. This is the source of the large area gZnO we observe. Zinc oxide preferentially forms at the interface between GO and Si (or SiOₓ specifically). The chemical identity of the layer is confirmed below. It is difficult to study rigorously why this phenomenon occurs, but I have come up with a few hypotheses. First is a difference in hydrophilicity. GO is very hydrophilic especially when compared with SiOₓ. This may cause GO to draw in more water than the Zinc precursor. However, a combination of SiOₓ and GO may draw water in along with the zinc precursor. Another possibility is the possible diffusion of species to the SiOₓ surface. Some material systems have seen diffusion of species through graphene in order to form thin samples.\(^9\) It would not be therefore unusual to see Zn species diffuse through the GO with a higher number of defects. However, there are two aspects that are left unanswered. First, there is not a clear driving force for Zn to diffuse to the SiOₓ surface. Additionally, if there was significant diffusion, it would be unlikely that the ZnO within the composite would remain that flat and regular. It is likely bulk pieces would form near defects in the GO, as the Zn would diffuse through these centers and be a point of agglomeration. Finally, there is the possibility that Zn acetate is attracted preferentially to SiOₓ. This may be due to the thermodynamic stability of Zn and the O in SiOₓ, causing Zn to naturally attach to the O sites. There may be other explanations, and many of them would be incredibly difficult to test. As such, it has been left to future study and speculation.

Atomic resolution imaging of the composites (Figure 2.9) provides some additional information. The STEM image, and corresponding intensity profile, shows clearly a 2-layer and 3-layer ZnO crystals between layers of rGO. This confirms the crystallinity of sub-nm sheets, and shows that the number of layers between rGO sheets is difficult to control exactly. The interlayer spacing of the ZnO is 0.25 nm, which is slightly less that the spacing for wZnO (0.26 nm) and within the values for gZnO (0.23-0.25 nm).\(^6\) The image also shows that the number of layers between ZnO and rGO is irregular, ranging from 1 to 4 layers.

As I observed later, side view images indicate gZnO is being made in between layers, so there is no doubt that the gZnO can be suspended using this technique. However, due to its small size, it is not suited for being suspended on its own over a hole in a TEM grid, making the residual carbon hypothesis of suspended nanosheets more plausible.
Figure 2.10: HRSTEM image of a gZnO/rGO heterostructure. a) HRSTEM HAADF image of the heterostructure showing a bright gZnO sheet (indicated by bright teal line) sandwiched between a darker SiO$_2$ (indicated by the green line) on Si and a darker contrast graphene sheet (indicated by a dark blue line). b) Colored elemental map of a portion of a). Individual element maps are labeled with their corresponding element. c) Low magnification HRSTEM image of the heterostructure, showing no contamination and near atomic flatness across a large area. The visible hole is from electron beam damage.

A fortunate accident allowed us to chemically verify the identity of the thin line definitively. Figure 2.10 shows a lamella in which the top composite layers, including the Pt, have been removed on accident, most likely a result of handling, leaving behind only the first layer of ZnO and GO. The ZnO appears thicker (~1 nm) most likely due to a combination of effects, including a loss of resolution in STEM-EDX due to a higher electron flux and slight misalignment of the zone axis combined with a relatively large thickness (>75 nm). EDX scans show a very clear strip of Zn exactly at the surface of the silicon, above the native oxide layer (highlighted by the extended O region below the composite) and below the GO layer. This confirms that the bright contrast at the interface contains Zn and is most likely ZnO. The STEM image in Figure 2.10c shows an extended region of this incredibly long and uniform gZnO feature, and is still only a portion of its true length. This measurement also shows a difficulty with imaging these samples. Figure 2.10c shows a hole in the sample appears as a break in the long-distance uniformity. This area shows a portion of the layer that has being actively damaged by the electron beam, in addition to a large carbon contamination buildup. As such, significant care must be taken during this side view imaging.

From these images and our top view imaging, it is clear that the gZnO has a relatively low concentration in the composite, making it difficult to study with typical measurement systems like UV-Vis spectrometry. However, the composite form can still provide information, as the concentrations of sub-nm samples are high enough for element specific measurements.
GIWAXS measurements

Grazing incidence wide angle X-ray scattering (GIWAXS) is similar to GIXD, but instead utilizes a 2D detector instead of a scanning 1D detector and has multiple advantages for our system over conventional XRD. Typical XRD systems cannot measure ultrathin nanosheets and cannot probe in plane scattering. It also cannot observe out of plane scattering of gZnO, due to the lack of long range order in the c axis direction. Our samples are also textured as synthesized, making it difficult to observe a true powder pattern. Other issues, such as strong GO diffraction limiting ZnO diffraction and a low concentration of ZnO in the composite, also remain. GIWAXS can probe in plane diffraction and its high x-ray intensity allows for the observation of low amounts of materials. Additionally, the grazing incidence allows the probing of our ultrathin composites and nanosheets. Measurements were typically performed at 0.1° for thick samples or 0.05° for thin samples, limiting the depth of measurement.

GIWAXS for various ZnO samples are shown in Figure 2.11. Thin composites correspond to morphologies similar to those found in A.1 that occur from blown-off or dilute dispersions on SiO$_2$ treated with O$_2$ plasma. Thick composites are similar to areas that are not blown off, typically with thicknesses of several hundred nanometers such that the gZnO/SiO$_2$ interface interactions are not probed. From our measurements on pure bulk ZnO synthesized from the template method, we observe a textured, powder like dispersion with strong out of plane components. This behavior is also observable in nanosheets, which is very unusual. Due to the ultrathin nature of these samples, there should be no out of plane components, or at least very weak components. It is highly possible that bulk crystals are also covering the surface and are producing significant scattering. The out-of-plane scattering is not observed in our composite samples, however, confirming their strong confinement capabilities. The scattering looks very convincingly from ultrathin nanosheets. From the radially integrated plots (Figure 2.12), the composite and nanosheet peaks are close to 2.2 Å$^{-1}$, which corresponds to a lattice spacing of 0.2855 nm that is near the gZnO lattice spacing. However, the bulk film synthesized from the template method also shows a much wider spacing. It may be that the bulk ZnO does not fully relax back to full wZnO lattice conditions, instead containing significant strain. In contrast, a reference bulk ZnO thin film shows a 2.27 Å$^{-1}$, which corresponds to 0.277 nm. This is below the expected value of 0.281 nm, but shows that my samples have a larger lattice parameter than a reference ZnO sample, which is consistent with gZnO formation. Although the change may be due to stress from the rGO or substrate, it at least shows promise for gZnO verification.

There are a few other interesting observations from the scattering plots. First, when compared with the thick composite, the nanosheets and ultrathin composite show stronger scattering. This seems to confirm that the interface layer and nanosheets on the surface are still crystalline. However, the out of plane diffraction is still puzzling, and the dominance of bilayer gZnO does not rule out an amorphous interface layer with the SiO$_2$. It may be a similar case to 2D GaN in which the first layer conforms to the SiC wurtzite structure and the subsequent layer relaxes towards a planar configuration.

The second interesting feature is the development of a secondary peak that appears for both the 100 and 101 scattering points, but not the 002. The secondary peak may be scattering from both gZnO and wZnO. It could indicate contributions from gZnO and residual bulk wZnO, as they should have different lattice parameters. However, the separation between the peaks does not correspond to the change between gZnO and wZnO. This may be indicative of an artifact caused
by bulk particles at slightly off planar directions are creating this secondary scattering. Since this doublet is sometimes viewed in bulk samples, this seems the more likely possibility. However, it may be indicating stress from the substrate, or uncertainty in the measurement. More experiments should be conducted to get a more complete picture.

Figure 2.11: GIWAXS Scatter plots of various ZnO samples. a) Bulk ZnO b) Thick composite c) Nanosheets d) thin composite. All scatterplots are scaled to the same intensity.
2.4 Chapter 2.4: XANES and fine structure verification

To obtain high precision information regarding the bonding configuration of these ultrathin samples, we utilized XANES measurements at the Zn L3 edge. A description of XANES and its utilization can be found in Chapter B.2. In brief, the photoelectron scattering from x-ray absorption is dependent on nearest neighbors and the availability of states. This means XANES can be used to determine coordination, bonding geometry, molecular orbitals, and the band-structure of a material. These all essentially affect the number of available states and their energies, which are the measured properties in XAS. Measurements were performed on a dispersion of mostly sub-nm samples on a Si/SiO$_2$ substrate. As controls, measurements were also taken from bulk ZnO and a composite of the alternating ZnO/rGO structure, where the rGO keeps the ZnO constrained as gZnO. The results are shown in Figure 2.13. The bulk ZnO spectrum matches other reports of XANES on wurtzite ZnO$^{99}$. In contrast, the thin composite and nanosheet ZnO show a markedly different spectrum, with a pronounced pre-edge peak and a shift to higher energies by about 1.2 eV. The enhanced pre-edge feature in gZnO is due to the broken Zn-O bond on the surface that leads to a change of local Zn coordination from tetrahedral into a pseudo trigonal planar environment. This phenomenon has also been observed in amorphous ZnO, as discussed in Ref. $^{99}$ which explains that the growth of Zn 4s pre-edge feature is attributed to stronger structural disorder in amorphous ZnO than in wZnO. The blue shift of this pre-edge feature, observed in gZnO with respect to wZnO, is likely due to the change of relative positions of Zn 4s states vs Zn 4d states. The thick composite also shows the pre-edge feature, but loses the bulk feature found near 1025 eV. This difference may be attributed to the substrate interaction. In addition, ZnO/rGO composite
and ZnO/SiO$_2$/Si nanosheet show almost identical spectroscopic signature, confirming the rGO has a negligible effect on the properties of the gZnO.

Figure 2.13: XAS of ZnO samples.

The most common interpretation method for XANES is typically to use standard references and create linear combinations of these standards in order to give a ratio of the quantity of each species. Each reference would ideally have a different geometry, level of hybridization, etc. which could then give the local coordination environment of the sample that was measured. There is no previous XANES measurement of gZnO or similar structures for Zn, so we cannot directly compare our spectra to a standard. One reference that does match well attributes the change to electron transfer between a carbon nanotube and a 3 nm film of zinc oxide on Fe$_3$O$_4$\textsuperscript{100}. However, our pure ZnO samples also shows this spectrum, making it unlikely that charge transfer is responsible for this change. In fact, it may be more likely that the carbon nanotube altered the threshold for ZnO to transform into a graphitic phase, since \( \sim 3 \text{ nm} \) is not far from the threshold. Alternatively, because the surface plays a larger role, signal from a relaxed surface may be contributing to the overall signal. It also does not match the thick composite structure, throwing doubt on the charge transfer or Zn-O-C bonding theory. In order to obtain more detailed information, I turned to theoretical studies provided by the Theory of Nanostructures group at LBNL. Details of the calculations are provided in B.3.

First, simulations are performed to determine the optimized structures of different phases under different conditions and then the spectra were calculated. The calculations for gZnO showed a lattice parameter of 3.4 Å and 2.32-2.38 Å, which has minor differences from experimental results due to simulated approximations. These hold relatively true for all systems. The XANES simulations for distinct atom geometries are then simulated, as the simulated spectra are for single atoms and not an entire crystal. In these simulations, typically there will be three types of atoms:
bulk atoms within the sheet, surface atoms, and interface atoms or the atoms that interact with the substrate. The spectra also are placed at an arbitrary eV value as reference, and later calibrated to a feature in the spectra. In that way, most of the simulation data start at 0 eV, and peak placements are compared. The optimized structures and their corresponding XANES spectra are detailed in the following sections.

The bulk ZnO simulated and experimental simulations matched well, indicating the simulated model was accurate (Figure 2.16). A four-layer gZnO sheet was first simulated (Figure 2.14). The first excited states, giving an idea of the shape of the states probed in the XAS simulations, for both bulk wZnO and the four-layer gZnO are shown in Figure A.7 and Figure A.8 respectively. Atom Zn19, a sub-surface atom, showed very little similarity to the gZnO spectrum, as there is a plateau where the peak should be. However, it does show the bulk like feature at, that appears in the gZnO and ultrathin nanosheet case. Atom Zn 30 shows a closer spectrum. A relatively broad peak appears, and the bulk feature is reduced. This broad peak is much lower energy and broader than the expected experimental pre-edge feature, but shares similarities to the pre-edge peak I observed in the experimental spectra. A majority of the following simulations hopes to elucidate the origin of that peak and possible reasons for the energy shift.

The next simulation mimics the composite structure. A simulated spectrum of a hypothetical gZnO/Graphene structure, based on the density functional excited core-hole approach,\textsuperscript{101} shows s-state characteristic of the pre-edge feature (Figure 2.15), which agrees well with previous spectroscopic analysis of wZnO and amorphous ZnO.\textsuperscript{99} A bilayer of planar gZnO (3×3 unit-cell) was initially sandwiched between two graphene sheets, and after structure optimization, the gZnO sheet is no longer perfectly planar, instead it becomes rippled such that almost half of the Zn atoms deviate from trigonal planar coordination as in the perfect planar gZnO to form tetrahedral coordination with 3 in-plane oxygen atoms and 1 out-of-plane oxygen, as shown in Figure 2.15c. The computed spectrum of bulk wZnO (black) and gZnO/graphene (red) are presented in Figure 2.15a, along with the experimental spectrum collected for reference wZnO (green) and thin composite gZnO/rGO (blue). The pre-edge feature is seen prominently in both. In fact, the thick composite matches the simulated spectra more accurately, as it also does not have a distinct bulk-like peak at 1025. Larger energy discrepancies of the Zn L-edge spectra are observed

![XAS Spectra of a 4-layer gZnO structure.](image)

Figure 2.14: XAS Spectra of a 4-layer gZnO structure.
for gZnO/graphene composite, where the pre-edge feature is red shifted in the simulated spectrum compared to experiment. The discrepancy may be related to the exchange-correlation functional used in the current calculation that fails to reproduce the relative position/hybridization between the O 2p states and Zn 4s/d states. Chapter B.3 provides more details about this discrepancy.

Figure 2.15: rGO/ZnO composite XAS simulations. (a) Simulated Zn L-edge XAS spectra with the experimental spectra as reference. (b) and (c) are the top and side view of a representative excitation state at ~ 1020 eV (indicated by red arrow) of bilayer gZnO that is sandwiched between two graphene sheets. Clear Zn 4s characteristic that is weakly coupled with nearby O 2p state is observed in the excited state plot.

Further simulations of composites agree with this analysis. Figure 2.16 shows simulated spectra from 7-layer wZnO placed between graphene layers. Structural models show only slight deviations from their normal configurations, with the ZnO retaining its buckled surface. From the simulations, wZnO still shows a bulk-like spectrum, indicating that bulk ZnO-graphene interactions are not a source for the pre-edge feature. A 4-layer is also simulated shown in Figure A.9 which goes into planar and buckled differences in more detail.
I also wanted to investigate possible effects by the substrate. Although there is difficulty, accurately simulating the amorphous surface of SiO$_2$, a close representation can suffice to observe any general changes. The structural model (Figure 2.17) shows a very distinct change relative to the isolated gZnO case. Here, the Zn bonds strongly to the surface of SiO$_2$. SiO$_2$ has a tetrahedral symmetry similar to ZnO, even in its amorphous phase. This acts almost as a template for the ZnO, causing the first layer of ZnO (Atom 108) to form a heavily buckled, near wurtzite phase at the interface. This indicates that interfaces can act as undercoordinated surfaces and create situations similar to planar surfaces. While there is enhanced buckling, the amorphous nature potentially forms some degree of psuedoplanar configurations which leads to a XAS spectra very similar to our previous results and similar to the amorphous ZnO reference. Alternatively, there are some strong interactions with the oxygen in SiO$_2$ that create additional effects. The two bulk layers (Atom 121 and 126) show spectra that appear very similar to the spectra of bulk-like ZnO. This buckling dissipates the farther away the atoms is from the substrate, settling somewhere between wurtzite and graphitic. The atom at the surface (atom 136), with a near planar structure, shows a pre-edge shoulder, indicating a return to the planar, undercoordinated surface. While a lot of information has been gained, none of the peaks have the same energy as the experimental value. It also cannot explain why the ZnO in the nanosheet and thin composite structures matches the composite spectra with a pre-edge feature. GO should have a completely different effect on ZnO, most likely creating a structure similar to isolated gZnO, due to its weak out of plane interactions. In this way, the two spectra should be markedly different, making it unlikely that SiO$_2$ contributes heavily to the ZnO behavior, or the structure has more relaxation than the initial simulations predict. However, since simulations show similar spectra, it may be coincidental. Similar measurements with hydroxyl coverage show no significant difference (Figure A.10).
Figure 2.17: XAS of 4-layer ZnO on SiO₂. Higher numbers indicate layers farther away from the surface.

Other simulations were attempted to find any anomalies. For surface structures in ambient, adsorbants can play a significant role in the structure. For these systems, hydrogen and water/hydroxyl groups are the most common as they are ubiquitous in nature. From the structural models in Figure 2.18, hydroxyl groups can cause a similar effect on ZnO as the SiO₂ substrate, with a formation similar to that of wurtzite ZnO, although with a stronger mixing of buckled and planar. Non-surface atoms show spectra very similar to the 4-layer gZnO non-surface atoms. The surface atoms, however, show a strong pre-edge peak intensity. The OH groups can act as bridges over the outermost oxygen on the outer surface. Once again, however, the simulated peak energy does not appear to match the experimental structure. This configuration is also relatively unlikely, as this simulates full coverage of water which would require a significantly humid environment.

Figure 2.18: XAS of gZnO covered by hydroxyl groups.
Strain was also considered as a possible mechanism for shifting energies or changing the overall spectrum, with the results shown in Figure 2.19. However, in-plane stress, both positive and negative, showed negligible energy shifts. It does, however, contribute to changes in the intensity of the peaks, which can possibly explain differences in observed intensities. For example, the 4s edge in the bulk ZnO spectra experiences an increase after a compressive stress and a decrease after a tensile stress.

![Figure 2.19: XAS of Bulk ZnO under tension. XAS spectra of an structurally optimized ZnO for both ZB and WZ. The slab under tension and compression is in-plane only.](image)

One last interesting consideration were the inclusion of oxygen vacancies in the bilayer gZnO sandwiched between graphene (Figure 2.20). These can provide an additional atom spectrum caused by a different type of symmetry breaking. The spectra all show low energy peaks. In fact, Zn51 shows a peak that is very close to the experimental energy. This is still unlikely to be the origin of the experimental structure, as it requires a very high concentration of oxygen vacancies to appear clearly in the experimental structure. However, it may point to edge effects, since there is a non-negligible amount of them from the small gZnO sheets in between rGO sheets.
Other possibilities exist, including possible edge effects or grain boundaries caused by the very small size of the initial gZnO samples that may contribute significantly. Ultimately, the symmetry breaking at the surface is recognized as the most common origin of the peak, and this symmetry breaking generally creates a relaxation towards a graphitic structure. Other configurations, such as the attachment to the SiO₂ appears to also form very similar pre-edge features, although the irregular structure does not exclude pseudoplanar configurations. This also does not explain the similarity in the pre-edge feature of both thin samples that have SiO₂ interactions and ZnO samples between graphene sheets. While the interface layer may require more investigations, based on the simulations of gZnO between graphene sheets, the samples between graphene oxide sheets are graphitic.

2.5 Optoelectronic properties of gZnO

2.5.1 Electronic structure of gZnO

XPS was used as an initial test to determine if the ZnO had undergone any electrical structure changes, which may hint at some changes in the bonding. XPS results, Figure 2.21a, show that the nanosheet ZnO shows an increase in the binding energy of the 2p peak relative to bulk ZnO by
approximately 0.5 eV. At first glance, this appears to be caused by an increase in the ionicity. This is a bit unusual, as most theoretical studies point to either a negligible change in ionicity, or a slight decrease. However, since these are nanosheets, there may be some quantum effects on the XPS spectra, which can lead to increases in the same way quantum confinement effects on the bandgap. Also worth noting, thick and thin composite ZnO shows almost the exact same increase in binding energy as the nanosheet. The thick composite shows only a slightly smaller shift, by about 0.1-0.2 eV. This seems to indicate that the GO does not affect the electrical structure of ZnO in any significant way, including charge transfer. The shift of the 2p peak will also become useful for obtaining the bandgap through XAS.

Figure 2.21: X-ray analysis of various ZnO samples. a) Zn 2p XPS spectra of various samples. The black dotted line indicates the peak position of bulk ZnO. B) Valence band XPS spectra of various ZnO samples and references.

Initial photoluminescence (PL) measurements (Figure 2.22) have also been performed to determine the optical characteristics and map the changes due to thickness and structural transformations. Above 1 nm, the PL signal is strong and is located close to the bulk bandgap of ZnO at 3.27 eV. As the thickness decreases, the PL signal blue shifts due to quantum confinement. The intensity drops with thickness, primarily as a result of a decreased absorption and emission. At 1 nm the signal is very weak and has blue shifted further. However, below 1 nm, the photoluminescence signal has completely disappeared. This may imply a very large bandgap increase below 1 nm, presumably larger than the 266 nm excitation energy of our laser, a transition from direct band gap to indirect band gap, or it may be caused by a lack of luminescence. It is also possible that the gZnO sheets have a fair amount of disorder due to the SiO$_2$, or the interactions with SiO$_2$ cause quenching. PL and cathodoluminescence (CL) measurements were attempted on composite structures, but no luminescence was detected, most likely due to quenching by the rGO and large absorption of the light and electrons by the rGO.
Figure 2.2: Photoluminescence of ZnO nanosheets.

In order to determine the band gap of the nanosheets, we turn to X-ray based techniques. Valence band XPS measurements were performed on a dispersion of primarily sub-nm samples to determine the valence band maximum (VBM) positions. As can be seen from Figure 2.21b, the ultrathin sheets and thin composite show a 0.8 eV shift to higher energies, determined from the crossing of the linear region of the spectra with the x-axis, when compared to the wZnO, and the thick composite only shows a slightly smaller shift. They also differ quite significantly from the SiO$_2$ substrate and rGO VB shapes, indicating that the signal does not come from the substrate or rGO.

From the XANES spectra in Figure 2.13, the peak at 1222 eV indicates that the 4s states of this phase are more available than those found in the wurtzite ZnO. The shift of the onset of absorption also indicates an upwards shift of the conduction band minimum (CBM), as it is formed by the Zn 4s states for both gZnO and wZnO. As the spectrum indicates transitions from the Zn 2p to Zn 4s states, the core level shifts must be taken into account. As mentioned previously, from XPS measurements (Figure 2.21) the Zn2p core binding energy shifts up approximately 0.5 eV from bulk to nanosheet. From the XANES data, the Zn 4s states shifts up approximately 1.2 eV, determined from the crossing of the linear region of the spectra with the x axis and, alternatively, using the shift in the first inflection point of the low energy part of the curve. Both methods agree within 0.2 eV. Therefore, the actual CB shift is about 0.7 eV to higher energies. The CBM and VBM locations of bulk wZnO and ultrathin gZnO, using known locations of the wZnO bands, are compared in Figure 2.23. From the band locations, the bandgap of ultrathin gZnO is found to be approximately 4.8 eV, which is significantly higher than bulk wZnO (~3.3 eV). This substantial change is consistent with theoretical predictions of the ultrathin gZnO band gap energy.
In order to directly measure the bandgap of gZnO, and since the PL and XPS/XAS showed very large changes in the band edge energies, low loss electron energy loss spectroscopy (EELS) measurements were identified as a strong candidate for bandgap determination. Composite structures are very stable under STEM conditions and contain primarily gZnO sheets. Figure 2.24 shows a low loss EELS spectrum of a composite structure. The most prominent feature appears as a peak at around 5-6 eV. This is the $\pi^*$ plasmon peak of GO, and typically ranges from 5-7 eV depending on the amount of reduction. Looking closer, a small, broad dip is visible near the apex of the peak. This is the contribution from the gZnO. Typically, the strength of plasmons are much stronger than contributions from bandgap transitions. Additionally, it is known that the gZnO filling of the composite is relatively low, adding to the very low signal compared with the plasmon peak. While it is unfortunate that the plasmon peak dominates the signal, it is still possible to obtain the information from the band transition through fitting. First, bandgap transitions from EELS data is fitted using a parabolic equation

$$ I(E) = I_0 + c\left(E - E_g\right)^{\frac{1}{2}} \quad (2.7)^{107} $$

Although this equation sometimes forgoes the $I_0$ constant, it seems appropriate for this case in which our signal is overlaid on a strong plasmon peak. This method, however, requires the subtraction of the background. The zero-loss peak is subtracted (Figure 2.24b), at least partially reducing the background for more accurate fitting. The spectrum is very noisy, so we implement a Savitsky-Golay 21-point smoothing function to better resolve the features. This filter is commonly used in spectroscopy, especially to combat high frequency noise. In particular, it works well with broad peaks and slow changing data, as is the case for the low loss EELS, especially when the filter width is much smaller than the smooth line profiles. The filtering greatly improves...
the visibility of the features, and greatly helps with any fitting attempts. Even without the fitting, it is clear that the edge will cross the line somewhere between 5 and 6 eV, which is relatively close to my previously calculated values. As before, we cannot be positive about the layer number this will belong to, but it does act as a secondary verification of the bandgap of the gZnO as a whole and that it greatly differs from bulk. The fitted curve in Figure 2.24c gives a value approximately 5.3 eV. The slightly higher bandgap relative to our X-ray techniques may be a result of Cherenkov radiation, which can occur in semiconducting and insulating samples. Essentially, the electron travels faster than the phase velocity of light, which can show a blueshift of the energy. Alternatively, the nanosheets within the composite tend to have be very small, such that it acts more like a 0D quantum well, like a quantum dot, which further pushes the bandgap to higher values due to quantum confinement effects.

2.5.2 Transport measurements

In order to capitalize further on the large area gZnO on an insulating substrate, I performed transport measurements using a two-probe configuration. Devices were fabricated using an electron beam lithography (EBL). A standard liftoff technique, in which photoresist is used to define the electrode locations, was used. Photolithography is difficult due to the optical transparency of the gZnO. However, because the position of the gZnO is known based on the composite location, the EBL alignment system can be used to fabricate electrodes at the precise location of the gZnO sheet. After the electrode patterns are developed, 5 nm Ti/80 nm Au contacts were deposited using electron beam deposition (EBD). The excess photoresist, with the unwanted gold deposited on top, is removed using an acetone soak. Initially, a two-electrode scheme was used, similar to other 2D material studies. However, instead of back-gating, ionic liquid gating (ILG) was used instead, utilizing DEME-TFSI as the dielectric media.

The transfer curve of sub-nm gZnO, Figure 2.25, was measured at 220 K utilizing the Oxford Telastron PT system, with a source-drain voltage $V_{DS} = 0.1$ V and a scanning gate voltage $V_G$ ($-1.0 \sim 8.0$ V). The resistance drops as a function of $V_G$ dramatically for more than four orders of magnitude, as shown in Figure S8B, indicating the obvious tuning effect of the electronic state of the gZnO by electric doping. The large resistance of gZnO ($\gg 10$ Giga Ohm) at the off-state of the transistor implies an unusually large bandgap, which is consistent with our X-ray based measurement results.
Due to the low carrier concentration, insulating behavior, and relatively poor crystalline quality, backgating using the thermal oxide is not strong enough to provide sufficient electrical signal. ILG, utilizing room temperature molten salts, can provide a much higher capacitance due to the formation of an electronic double layer. Because the charge carriers in the ZnO (electrons) cannot penetrate into the ionic liquid and the ions cannot penetrate into the ZnO, the potential drop occurs only over a 1 nm distance, creating a huge capacitance. This helps to create massive increases in the electron concentration in the ZnO, allowing electrical characterization. Our channel length is approximately 2 µm, with a roughly 7.5 µm width. From Figure 2.25, signal only becomes detectable after 1V is applied to the gate. The on-off ratio for resistance is only about $10^5 - 6$. This is comparable, or slightly less than a typical on-off ratio for 2D materials. However, it is a few orders of magnitude lower than state of the art devices. In the two-terminal configuration, the mobility, $\mu$, and electron concentration, $n_e$, can be determined by the following equations.

$$\mu_e = \frac{L * g_m}{W * C * V_{ds}} \quad (2.8)$$

$$n_e = \frac{V_{th} * C}{q} \quad (2.9)$$

$$g_m = \frac{dI_{SD}}{dV_G} \quad (2.10)$$

$V_{th}$ is the threshold voltage, which is defined by the voltage at which there is observable current above baseline in the $V_G$ vs $I_{SD}$ curve. This occurs at about 5V in our system. $C$ is the capacitance of the IL (~2.7 µF/cm² fore DEME-TFSI at 0.1 Hz), $L$ is the length of the active channel (2µm), and $W$ is the width of the active channel (6 µm). $q$ is the charge of the carrier. $g_m$ is the transconductance, which is the slope of the source drain current versus the gate voltage. From the data, I obtained a mobility of $1.63 \times 10^{-2}$ cm²/Vs and an electron concentration of $8.43 \times 10^{13}$ cm⁻². The mobility is most likely slightly overestimated, as the capacitance used was not under true DC conditions. However, with such a low frequency, the true DC capacitance would not be much higher as the relaxation time of the ionic liquid is typically not greater than a few hundred of seconds. The mobility is quite poor, on the order of amorphous silicon. This will drastically limit the potential applications for gZnO, especially if it were to be used in high temperature applications in which phonon scattering becomes more severe. Several improvements can be explored to improve the performance.

First, since gZnO is a highly ionic material, it will most likely be strongly affected by the SiO₂ substrate. Even 2D materials with primarily covalent and Van der Waals bonding have very...
significant changes in their electrical properties by either making freestanding samples or choosing an appropriate substrate. I expect a similar improvement in the gZnO electrical parameters. This could be accomplished by etching the SiO$_2$/Si with XeF$_2$ to create a freestanding channel.

Second, gZnO is naturally insulating and has a very low carrier concentration. This can be remedied by Al doping, or similar elements. Theory predicts Al will still act as a donor for gZnO and our EDX results showed that Al can be incorporated using the GO template synthesis technique. This will hopefully increase the conductivity enough that electrical current could be detected with either no gate or solid dielectric gates. Alternatively, inducing oxygen vacancies may prove a useful technique for increasing the conductivity. This would allow us to test the high temperature device potential of gZnO.

Finally, the mobility is adversely affected by the low crystalline quality/nanocrystallinity of the gZnO. This is much more difficult to remedy but would significantly decrease scattering by grain boundaries and other defects.

There are also practical device concerns. The mobility presented here represents a lower limit due to contact resistance. Due to the huge change in the conduction and valence bands, the work functions of our contact metals may not be appropriate for good ohmic contact, leading to a large contact resistance. Additionally, 2D materials tend to have poor top contact in general due to the low thickness, weak contact due to Van der Waals interactions, and the possibility of contamination. Annealing briefly in Ar/H$_2$ or vacuum can help facilitate better contact and improve performance of these devices.

### 2.6 Alternative substrates and transfers

Much of graphene’s usefulness stems from its ability to be synthesized on multiple substrates and in solution, and its ability to be transferred between arbitrary substrates. Typically this is performed by etching away the substrate, as is the case for exfoliated graphene on a thermal oxide wafer, using KOH, or CVD grown on copper, using FeCl$_3$ or similar etchants. However, there are many other clever and sophisticated methods, although they may require additional tools not readily available. I also wanted to explore options for synthesizing and transferring ZnO to arbitrary substrates. This is of particular importance after FIB investigation, as it is easiest to utilize the complete layer near the interface for additional characterization and application. Also, attempting growths on other substrates may provide information about the mechanism for growth and the high affinity of the gZnO for the interface of SiO$_2$ and GO.
The most obvious solution would be to grow the ZnO between the interface of GO and graphene. In this way, graphene could be burned away, similar to how GO is removed. However, my FIB results (Figure 2.26) showed no indication of a complete ZnO layer in between GO and graphene. Many partial flat layers are visible near the interface, but they typically are very short, similar to what is observed within the composite. It is also peculiar that the graphite/SiO$_2$ interface and graphite/composite interface both show a slight gap. This is not observed in composite FIB samples. It may be a trapped layer of contamination, but typically annealing graphene tends to group the contamination together to form good interfaces. EDX results in Figure 2.27 show one additional interesting result. ZnO does not diffuse into graphene or diffuse to the graphene/SiO$_2$ surface. This confirms that this growth method does not rely on diffusion through the defects, as is the case for GaN,\textsuperscript{75} and GO is necessary for this method. This is further confirmed by the observation of an interface layer in an intercalated composite structure that had not yet been heated in Figure A.16.
Given this information, it is possible that the oxygen in SiO$_2$ allows the interface layer to form. Other oxide substrates, such as Al$_2$O$_3$, could be used provided they were sufficiently flat. The main challenge of a pure oxide substrate is the processing in a FIB, as the gallium beam and insulating substrate creates significant charge buildup which prevents lamella fabrication. There are methods to counteract this, and it may be worthwhile to attempt this synthesis on ultraflat quartz, Mica, or alumina.

As a simultaneous test of forming 2D metal oxide heterostructures and interface growth conditions, I attempted to grow ZnO on top of Fe$_2$O$_3$. As seen in Figure 2.28, a bright line appears at the interface, similar to pure ZnO or Fe$_2$O$_3$. HRSTEM imaging would be preferred to resolve the layer and determine if it had a ZnO layer and then an Fe$_2$O$_3$ layer, since the comparative contrast of Fe$_2$O$_3$ is not significantly different from rGO and ZnO to be indistinguishable from both at the same time using Z contrast. However, the relatively disordered surface and polycrystallinity makes atomic resolution challenging. From EDX measurements, the Zn and Fe signals both increase at the same time, just before the C signal, showing that it is at the interface between SiO$_x$ and rGO. Although the resolution of the EDX is not sufficient to clearly differentiate between two different layers, it typically can resolve small changes in the initial increases. Therefore, it is highly likely the two layers have mixed, unsurprising considering the high temperatures and thermodynamic instability of stacked nanolayers of non-layered materials. However, it still forms an interface layer and this may be used to create alloyed nanolayers, and heterostructures between the alloyed nanolayer and the rest of the composite. Additionally, the spectrum shows a tail in the Fe peak, potentially indicating slight diffusion into the composite. In this case, a gradient index material may form, which can be useful for optical applications.
Figure 2.28: ZnO composite grown on a thin layer of Fe₂O₃. a) STEM image of the composite sandwiched between Si (left) and Pt (right). B) EDX linescan integrated vertically along the green box in a). A truncated HAADF STEM image is shown at the top and the counts of each element at a given position at the bottom and is aligned with the top image.

Transfer of the ZnO sheets is more difficult. ZnO is amphoteric, so it will dissolve relatively easily in any acidic or basic solutions. In this way, the most common transfer method for SiO₂, utilizing KOH, is unsuitable. Additionally, ZnO appears to be more solidly attached to the substrate than typical 2D materials, making many other schemes that do not utilize etching unsuitable. Metals and polymers can utilize less powerful chemicals than those required for SiO₂ etching. However, this growth method also runs at high temperatures, such that polymers, due to burning, and metals, due to roughening and diffusion, are not able to be utilized. NaCl substrates are also popular, as they can release films by dissolving in water, but due to the aqueous solution used for synthesis, they cannot be used. As such, dry etching appears to be one of the few options remaining. Typical plasma etching systems typically can sputter materials and the common chemistries will either etch ZnO or will not be able to etch SiO₂. However, one method utilizes only XeF₂ gas. These systems can etch Si and SiO₂ at finite rates without etching ZnO, or at least ZnO will etch extremely slow. It is also an isotropic etch, meaning it can create undercuts below the ZnO, possibly creating a suspended structure.

2.7 High temperature annealing of gZnO

Due to its chemical stability and oxidation resistance, gZnO shows great potential for applications at high temperatures in ambient or oxidative environments. I proceeded to test the high temperature behavior of ZnO sheets of different thicknesses. The samples are imaged using AFM and SEM before and after a 1 hour anneal in air at 800°C. SEM images and RMS roughness values, shown superimposed on the corresponding sample, before and after the 800°C annealing are shown in Figure 2.29a and b respectively. From the SEM images, it is clear that after the 800°C anneal, area A and, more noticeably, area B show an increase in the roughness and a coarsening to larger particles. The streaks are caused by a charging effect that was enhanced due to the coarsening effect, i.e., it breaks the continuous film and increases the thickness of low conductivity ZnO. RMS values from AFM measurements confirm a significant change in the roughness. On the other hand, the thin sheet, area C, remains flat and thin, and is comparable to the substrate roughness. The sub-nm thickness, and low roughness, is confirmed in the linescans shown in
Figure 2.29c and d and the AFM images in Figure 2.29e and f, while the roughening of thicker nanosheets is exhibited in Figure 2.29g and h. It should be noted that the slight decrease in the substrate and area C RMS values with annealing temperature may be a result of high temperature smoothing of the surface, such as the case seen in silicon wafers.\textsuperscript{115} I believe that the different experimentally observed roughening (or lack of) behaviors are due to the surface energy differences between gZnO and its bulk counterpart. Due to its layered structure, the \{0001\} surface has a very low surface energy and it is unlikely to undergo coarsening or ripening to reduce the surface energy.\textsuperscript{116} The wurtzite phase, however, has a high surface energy from unfulfilled bonds and a large dipole energy, so the nanosheets will ripen and coarsen to thicker nanoparticles at high temperature, which has been observed and reported previously for wurtzite ZnO films.\textsuperscript{117} This high temperature robustness of gZnO is very different from most 2D materials, such as graphene or transition metal chalcogenides, that tend to oxidize and/or decompose at elevated temperatures in ambient conditions. This allows gZnO to be a promising 2D candidate for high temperature ambient environment applications. At temperatures greater than 800°C, some roughening is observed in the gZnO nanosheets. However, instead of coarsening, pockets appear that seem to indicate partial evaporation of the gZnO. Further tests should be performed to understand this behavior.
Figure 2.29: High temperature annealing of ZnO nanosheets. SEM images of a) as synthesized nanosheets and b) nanosheets annealed at 800°C with corresponding roughness values. c) and d) correspond to linescans shown in a) and b) respectively. Lettered regions indicate areas of different thicknesses: A = 6 nm, B = 1.5 nm, C = 0.54 nm, sub = Si substrate. Scale bar is 2 μm. AFM images of the sub-nm ZnO sheet e) before and f) after the 800°C anneal showing no increased roughening. AFM images of the 1.5 and 6 nm nanosheets g) before and h) after the 800°C anneal showing a massive increase in roughness. The pre-anneal roughness values are based on the background flat sheet and excludes the large particles sitting on top.
FIB composite samples were also investigated after high temperature anneals in vacuum. Figure 2.30 shows a composite structure after 700°C synthesis. Interestingly, many sub-nm features still remain, with only slight changes in the length of segments. This implies diffusion is very limited in these systems, even at higher T. However, additional images show the emergence of long nanosheets that are above the threshold, around 2-3 nm thick. However, these also remain very straight and flat. This seems to imply that high temperature stability in the composite is not limited to gZnO. This implies that during synthesis, GO acts as a barrier to diffusion in and out of plane. The thickening of these plates is noticeable, but they do not form discrete nanoparticles. GO appears to slow surface diffusion and protects the front surface from atoms. However, this still is a marked difference when compared to nanosheet behavior. The thickening of many nanosheets show that some diffusion is still present due to the availability of Zn. In the nanosheet case, there is no Zn source near the surface, only near its lateral edge where the diffusion would need to travel a much greater distance. Additionally, the similar density of ZnO shows that GO may prevent evaporation of Zn annealing in vacuum, which was observed in nanosheet samples without GO.

2.8 Graphene oxide removal at lower temperature

The use of high temperatures in air can be detrimental to many different types of substrates. Typically, this causes significant oxidation or causes a large amount of roughening, as is the case for metallic films. Additionally, it requires an immense amount of energy and time, making it less economical and much more inconvenient for rapid study. As such, I looked for an alternative method for removing the GO while keeping the integrity of the ZnO. A paper that has many similarities to ours, although developed separately, utilizes a hydrogen plasma to remove graphene off of layers of GaN that were encapsulated by the graphene. Hydrogen was used to prevent the oxidation of GaN, which is fairly sensitive at very low thicknesses. In our case, ZnO is not sensitive to oxidation, and it is possible to use the much more common oxygen plasma to remove the GO.
At first, RIE was used to determine the resilience of ZnO to the high energy plasma, as some sputtering still occurs. First, I took an AFM image of a ZnO sheet, shown in Figure 2.31. The roughness values of the ZnO is roughly the same as the substrate and similar to other observed gZnO nanosheets. Afterwards, I placed the sheets into an RIE chamber and exposed it to an O\textsubscript{2} plasma at 60 W with 20 sccm O\textsubscript{2}. After 2 minutes of RIE time, which is much longer than necessary to remove one or two layers of GO, the AFM of the gZnO nanosheet shows no signs of degradation. The roughness remains roughly the same (0.160 nm before vs 0.127 nm after) and the edges show almost no signs of retreating, especially considering the relatively long RIE time. This means ZnO can survive an oxygen plasma, opening up the possibility of using plasma to remove the GO at lower temperatures.

![AFM images](image)

Figure 2.31: RIE treatment of ZnO. a) Before and b) after RIE O\textsubscript{2} cleaning.

Using the FIB sample from before with only a single ZnO/GO bilayer, we can see how well this process works in practice. In this case, the sample was subjected to a plasma cleaner with a mixture of 80\% Ar, 20\% O\textsubscript{2} for 45 seconds. The plasma cleaner should actually be gentler than the RIE, as it does not utilize directional guidance of the plasma to induce additional sputtering. From Figure 2.32, it can be seen that the C layer that used to be on top of the ZnO has disappeared. The only carbon signal is from carbon contamination, as can be seen by the fact that the signal is homogeneous over the entire sample. The ZnO signal remains as a very clear \~1 nm strip on the surface of the SiO\textsubscript{x}. Some broadening occurs, most likely due to even less protection from high flux STEM-EDX scans. There may be some slight damage caused by the Ar, since it is more likely to sputter, but it is not very significant. This confirms the use of oxygen plasma as a way to remove the GO.
Figure 2.32: Side view image of Ar/O₂ plasma cleaned sample. The center image is a STEM-HAADF image before cleaning as a reference for the before and after images. Before cleaning images on the left show a C layer, which is absent in the after-cleaning images on the right.
Chapter 3  Graphite oxide template synthesis of Fe$_2$O$_3$ nanosheets and composites

Hematite iron oxide ($\alpha$-Fe$_2$O$_3$) is the most common form of iron oxide, found widely in nature, usually in rock and soil, and typically being the most thermodynamically stable, fully oxidized form. Its hydrated form is the most common component of rust. It crystallizes in the rhombohedral crystal structure as corundum, similar to alumina, in which O ions form a hcp structure and Fe$^{3+}$ ions occupy 2/3rds of octahedral interstitial sites. It has an indirect bandgap of 1.9-2.2 eV, although direct bandgaps have also been observed.$^{118,119}$ It is weakly ferromagnetic/ferrimagnetic or antiferromagnetic at room temperature due to canting (or tilting) of the magnetic moments caused by the spin-orbit coupling behavior from low symmetry of the Fe sites.$^{120}$ Furthermore, above 956 K it is paramagnetic,$^{121}$ and below ~ 260K it experiences a Morin Transition which leads to a loss of a magnetic moment.$^{122}$ The Morin Transition occurs because the canting is no longer energetically favorable at lower temperatures, causing a realignment along the c-axis.$^{123}$ Fe$_2$O$_3$ has very high coercivities (up to hundreds of mT), making the magnetism quite stable albeit weak.$^{124}$

![Figure 3.1: Basic info on iron oxides with a focus on hematite. a) A schematic of some of the many applications for iron oxides. B) Crystal structure of $\alpha$-Fe$_2$O$_3$ (hematite). The structure between the green/orange and orange/blue lines indicate two different proposed crystal structures for hematene. Adapted from reference 125.](image)

This material has been studied heavily for photooxidation of water, photodetectors, photoanodes, and solar cell applications due to its moderate band gap, abundance in nature, low cost, nontoxicity, and stability in various environments including water. However, it does suffer from a short hole diffusion distance, typically considered less than 20 nm, and a short charge carrier lifetime and low mobility of photogenerated charge carriers.$^{126,127}$ Many of these disadvantages can be overcome by nanostructuring such that the charge carriers only need to diffuse through a few layers of material to reach the outer surface.$^{127,128}$ Nanorods of Fe$_2$O$_3$ have shown particular success with enhanced photoelectrochemical cell performance$^{129,130}$ when compared with nanoparticles because of its lower surface area which leads to higher mobilities and lower charge recombination rates.$^{131}$ This does not help along the axial direction of the nanowire, but still greatly reduces the diffusion distance in the radial direction. This still has limitations, both because the nanoparticle size must be very small and polycrystalline nanostructures still suffer from a high charge recombination rate because of boundaries between the particles. Nanostructuring has also found benefits in Li ion batteries,$^{58}$ and increased sensitivity to formaldehyde gas.$^{132}$
In addition to nanostructuring, α-Fe2O3 has been combined with charge-extraction layers, such as cobalt/phosphate catalysts, IrO2, or rGO\textsuperscript{133–135} to improve water splitting performance and reduce losses. As mentioned previously, the high durability and fantastic conductivity of graphene or rGO make them particularly good candidates for conductive layers for Fe2O3. This was confirmed by transient absorption and time-domain terahertz spectroscopy that proved charge carriers could transfer from the α-Fe2O3 into the rGO, where they were free to move and, because they were trapped in the rGO, they could not recombine.\textsuperscript{134} In previous work, nanoparticles with an average size of 40 nm were used.\textsuperscript{58,134} This is nonideal, as there is still a significant amount of diffusion from the center portion of the nanoparticle and a reduced specific surface area. Synthesizing atomically thin two-dimensional sheets of iron oxide would maximize surface area for absorption while maximizing the interfacing with rGO acting as the carrier extraction layer and reducing the diffusion distance to well below the diffusion length. That is a primary goal for my work on Fe2O3 nanosheets and composites.

Section 3.1 will show optical and AFM images of the Fe2O3 sheets and highlight their differences to gZnO. Section 3.2 will be dedicated to crystallography studies using composite structures and the apparent changes induced by the rGO using TEM and GIWAXS. Section 3.3 presents XANES spectra of composite structures and the significant changes in the electronic structure. Section 3.4 will present optoelectronic studies of Fe2O3. Section 3.5 will explore some changes in the magnetic properties.

### 3.1 Optical, AFM, and SEM imaging of Fe2O3 nanosheets

The growth procedure is nearly identical to the gZnO, except with an iron precursor (Iron nitrate nonahydrate (Fe(NO\textsubscript{3})\textsubscript{3–9H\textsubscript{2}O)). Additionally, the argon bake is performed at 600°C. It should be noted that these nanosheets will not be a van der Waals material like gZnO or other 2D materials. As such, exfoliation is not the preferred method for synthesizing nanosheets. There has been some success for hematite and other materials, but the results are often poor\textsuperscript{136,137} or the method is specific to certain materials.\textsuperscript{138} Figure 3.2 a and b show an SEM and AFM image of a Fe2O3 nanosheet. From the corresponding linescan in Figure 3.2c, the sample surface is incredibly flat and shows a thickness of approximately 0.56 nm. This corresponds to a partial unit cell of Fe2O3, much in the same way a bilayer of gZnO is a partial unit cell of wZnO. This partial unit cell may have a similar structure to reference\textsuperscript{40} and \textsuperscript{137} that shows a half unit cell structure recently dubbed hematene (roughly outlined by the dotted lines in Figure 3.1B) or may be similar to Fe2O3 surface structures.\textsuperscript{139} The hematene thickness is about 0.398–0.56 nm when textured in the [001] direction. When placed on a substrate, the total height from the substrate to the top of the sheet could roughly be 0.56 nm, as seen in my results.

Figure 3.2e and f show an optical image of an rGO/Fe2O3 composite before and after calcination. Unlike the gZnO nanosheets, the Fe2O3 nanosheets are visible. This is, once again, due to the differences in refractive indices between ZnO and Fe2O3. Fe2O3 has a much larger real part of the refractive index (minimum value of 2.475 at 400 nm) and a nonzero imaginary refractive index (peaks to 1.1 at 400 nm and reaches a value of 0.06 near 700 nm). Fe2O3 has a dispersion much closer to graphite. When placed in the same calculations as ZnO, the contrast is much higher, up to 15% at 550 nm. It behaves similar to BN in that it has positive and negative contrast over the visible range that gives an overall weaker contrast in white light conditions.\textsuperscript{91} However, it retains enough contrast to remain visible in optical microscopes, albeit quite weakly. In the composite image, three distinct layers are clearly visible. However, they are nearly impossible to resolve in
the nanosheet images, indicating a much weaker contrast than what is expected from the calculations. This weakness may be a result of large changes in the optical properties due to quantum confinement or size effects. From the AFM image in Figure 3.2g, the three distinct half nm steps are visible. These three layers correspond well to the three layers observed in the composite structure, indicating that the additional half-nm sheets originate from between GO sheets, similar to the case of the gZnO.

Figure 3.2: Fe$_2$O$_3$ nanosheets and composites. a) SEM and b) AFM image of a half-nm Fe$_2$O$_3$ nanosheet. c) Linescan of the white dotted line in b) showing the height of the nanosheet. d) Optical image of an Fe$_2$O$_3$/rGO composite and e) pure Fe$_2$O$_3$ nanosheet after calcination. f) AFM image and g) corresponding linescan of the nanosheet in e).
3.2 Crystallographic Studies of Fe$_2$O$_3$ and Composites

3.2.1 Raman spectroscopy

My ZnO previously had difficulties with Raman with conventional wavelengths (i.e. visible) due to the lack of resonance Raman and a nanograin structure. However, Fe$_2$O$_3$ has a bandgap near 2 eV, which is much closer to visible wavelengths. Raman was still unable to produce signal from very thin nanosheets, but it was able to return signal from relatively thick composite structures, as seen
in Figure 3.4. All strong peaks for Fe₂O₃ and rGO are observed in the composite, while only Fe₂O₃ peaks are observed in the bulk structure. Indeed, the Raman spectrum of bulk hematite Fe₂O₃ matches well to the composite structure and to literature. The composite structure also shows the Fe₂O₃ peaks, except with slight shifts of the peaks to a lower wavenumber. The shifts also are all different magnitudes, potentially pointing to anisotropic effects from the rGO or nanostructuring. The A₁g mode has the smallest shift, from about 220 cm⁻¹ to 218 cm⁻¹. The E₉(2) mode shifts from 290 to 283 cm⁻¹. The largest shift belongs to the E₉(4) mode, which shifts from 409 cm⁻¹ to 399 cm⁻¹. This is distinctly different from the measured hematene Raman, and is most likely due to contributions from the rGO. These results may be from structural changes (view GIWAXS data) or electronic changes (view XAS data) or both. It is unlikely to be purely due to a compressive stress, as these increase the wavenumber value. Although a tensile stress is unlikely given the confinement should lead to compressive stresses, it would cause the correct shifts. Additionally, for comparison purposes, the E₉(2) mode shifted roughly 30 cm⁻¹ under 55 GPa of isotropic pressure, and about 7 cm⁻¹ under 10 GPa of pressure.

3.2.2 TEM imaging

Figure 3.5: TEM characterization of Fe₂O₃ composites. a) HAADF-STEM image of a rGO/Fe₂O₃ composite. b) NBED diffraction image of the sample in a). c) Side view TEM image of a composite.

Similar to the gZnO case, I assumed a non-uniform filling of the graphite oxide. As such, I started with NBED diffraction imaging. Figure 3.5 summarizes the TEM characterization of Fe₂O₃ composites. Figure 3.5a shows a normal STEM image of the composite and Figure 3.5b shows a weak polycrystalline Fe₂O₃ ring inside of a mostly single crystal GO sample. The ring shows the 110 scattering of Fe₂O₃ (d = 0.25-0.26 nm). This confirms the crystal formation within the GO matrix, confirming the results of the Raman measurements. A more interesting result is seen in the side view image shown in Figure 3.5c. Because of the much lower average Z value for
Fe$_2$O$_3$ compared to ZnO, the Fe$_2$O$_3$ contrast is much weaker in STEM imaging, making layer observations more difficult. However, similar to the ZnO case, an interface layer is seen with a higher contrast relative to the native oxide layer. Between this and the layering seen in the AFM imaging, it can be inferred that the Fe$_2$O$_3$ normally forms as roughly 0.5-1.5 nm thick sheets. In fact, there is one other observable layer that shows a roughly 1.5 nm thick sheet deeper in the composite, showing that large nanoparticles would be visible. The absence of visible nanoparticles strongly suggests the formation of ultrathin nanosheets. In any case, it is obvious Fe$_2$O$_3$ demonstrates confined nanosheet growth.

### 3.2.3 GIWAXS measurements

For Fe$_2$O$_3$, we do not expect as drastic of a change in the structure. However, distortions in the structure may still occur for very small structures, reported as a possibility in,\textsuperscript{40} or caused by stress from the rGO. Figure 3.6b, displays the bulk reference GIWAXS 2D scatter plot and Figure 3.6d shows a thick composite structure. The bulk reference spectra show typical powder hematite scattering. Radial integration plots of both a thin composite and bulk Fe$_2$O$_3$ are shown in Figure 3.7. Only the thin composite is shown in Figure 3.7, as it has a sharper peak than the thick composite which is shown in the Figure A.12. The bulk plot shows a 110 scattering vector around 2.51 Å$^{-1}$, corresponding to a d spacing of about 2.5 Å, as well as additional hematite peaks. In contrast, the composite only shows scattering from the 110 vector, similar to the case of gZnO. Interestingly, the 110 scattering from the composite still shows a powder profile. It is expected to be textured since there is no visible diffraction from a z-direction set of planes (ie 103) and the rGO itself is heavily textured. Since thin composites (Figure 3.6c) show texturing, it may be formation of some nanocrystals with random orientation or some contribution from wrinkles and other stacking defects that is more likely to occur in thick composites. It may be more noticeable in the iron oxide due to a higher intercalation efficiency and a higher amount of Fe$_2$O$_3$ in the composite as compared to ZnO. From the radially integrated plots, both thick and thin composites show a decrease in the lattice scattering vector to around 2.45-2.47 Å$^{-1}$, meaning the lattice spacing has increased to about 2.55 Å. This corresponds to roughly a 2-2.7% strain. This shift would be consistent with an in-plane tensile stress. It is possibly due to an out of plane compressive force caused by the GO as the Fe$_2$O$_3$ formed crystals, as the GO is essentially encapsulating the Fe$_2$O$_3$. This compression in the z-axis caused the in-plane lattice spacing to increase. Alternatively, there may be a structural distortion similar to the observed in ref.\textsuperscript{40} In addition, thin composite Fe$_2$O$_3$ shows sharper crystallinity, like the ZnO case, confirming the crystallinity of the interface layer. One other interesting observation is that bulk Fe$_2$O$_3$ shows a full relaxation to the expected literature values of normal Fe$_2$O$_3$ conditions, while the bulk ZnO that remains distorted. It is unknown why this occurs.
Figure 3.6: GIWAXS Scatter plots of various Fe$_2$O$_3$ samples. a) Nanosheets and c) a thin composite with logscale intensity (arbitrary unite). b) Bulk reference and d) thick composite scatter plots.
3.3 Optoelectronic properties

3.3.1 Absorption

From the success of Raman measurements on Fe$_2$O$_3$ composites, I anticipated that the UV-Vis spectroscopy would also prove fruitful. After collecting the reflection and transmission spectra, the absorbance spectra of a composite structure and a reference rGO sample were obtained using the following equation,

$$\text{Abs}(E) = \ln \left( \frac{1 - R(E)}{T(E)} \right)$$  \hspace{1cm} (3.1)

Indeed, from Figure 3.8, there is increase in the UV absorbance of the composite when compared with rGO. It also appears that the composite shows an earlier onset of absorption and a kink at around 380 nm. Because the Fe$_2$O$_3$ absorption is relatively weak and the edge is near the region over which the strong absorption peak from rGO C-C bonding network absorption lies,\textsuperscript{142} it is difficult to deconvolute the two contributions to the absorption and discern the bandgap using
conventional linear extrapolation. However, the onset of absorption can give a rough idea of the lower bound value. Typically, a linear extrapolation is used to determine the bandgap of a material using the absorbance. At higher wavelengths than the kink, there appears to be a somewhat linear region that differs greatly from the composite structure. This may be strong contributions of the Fe$_2$O$_3$ combined with the rGO absorption. From the crossover between the linear region stemming from the kink and the constant absorption from the rGO, the value can be estimated as $\sim 2.4$ eV. Once again, it must be stressed that this is a rough estimate due to the strong rGO absorption obscuring the real values. The only information that can be sure is that there is no significant absorption from Fe$_2$O$_3$ before $\sim 550$ nm. Hematene values were determined to be near 2.2 eV, although the exfoliated layers were not perfectly monolayer and bulk contributions may lead to a lower bandgap determination.$^{137}$ Additionally, band gaps for hematite Fe$_2$O$_3$ nanorods have shown values between 1.95 -2.35 eV for the direct bandgap and 1.38-2.09 eV for the indirect.$^{118}$ Bulk values also seem to differ significantly based on preparation method.$^{118}$ The large increase I observe also may be due to a Burstein Moss shift that increases the optical bandgap due to an a large charge transfer filling the CBM. More details on this charge transfer are discussed below.

![Absorbance spectra](image)

**Figure 3.8:** Absorbance spectra of rGO and an rGO/Fe$_2$O$_3$ composite. The arrow indicates a kink, followed by the linear region indicated by the dotted line.

### 3.3.2 XPS

Similar to the ZnO samples, I wanted to observe the changes in the core levels. From the XPS measurements in Figure 3.9, composite structures have significantly lower binding energies than their bulk counterparts, up to 0.5 eV. This shift indicates a charge transfer from the rGO to the Fe$_2$O$_3$. This is different than the ZnO case which shows increases for all nanostructures.
It is very interesting that the Fe$_2$O$_3$ behaves very differently in the composite than ZnO. ZnO shows the same XPS and XANES spectra from nanosheets and a composite, showing that the GO has very little influence on the gZnO. This should be expected, as gZnO will behave more as a 2D material that, despite having ionic contributions, does not have many dangling covalent bonds and a low surface energy. In contrast, Fe$_2$O$_3$ shows a strong difference between its composite and nanosheet spectra. The XPS of the composite shows a strong shift to lower energies, while nanosheets show a marked increase, similar to ZnO. The increase in energy from nanosheets is consistent with the quantum confinement induced increase or potentially interactions with the substrate. The shift to lower energies indicates that Fe$_2$O$_3$ gains electrons. Typically, this can either mean a change in oxidation state or a simple charge transfer, in this case from rGO. Fe$_2$O$_3$ has many more dangling bonds, which are more likely to be passivated from rGO. From Raman and diffraction experiments, only Fe$_2$O$_3$ signatures appear, implying that it is more likely a charge transfer. While it may also be an increase in oxygen vacancies due to a lower partial pressure of oxygen in the system during synthesis, it is unlikely due to a strongly oxidizing environment in the rGO. This implies that the behavior of these ultrathin nanosheets in the composite structures depends heavily on the properties of the specific intercalated material. While this may be obvious, it is a departure from common composites that tend to mechanically mix the bulk nanocrystals with GO or graphene or synthesize the crystals in a mixture with GO. In these cases, GO has a negligible effect on the material, as the sizes are large enough for the bulk contributions to be large and the synthesis is performed in an environment dedicated to the nanocrystal formation.

![XPS graph](image)  
**Figure 3.9**: XPS of various Fe$_2$O$_3$ samples. The blue dotted line shows the peak position of bulk Fe$_2$O$_3$ and the red dotted line shows the location of the nanosheet peak position. The unusually low nanosheet XPS is most likely due to sample-to-sample differences and inconsistencies in making the thin samples by blow-off or tape removal.
3.4 XANES Spectra of Composite vs Bulk

Unlike Zn, iron has multiple oxidation states, causing its XANES spectra to be very sensitive to oxidation state changes and charge transfer. While some of the changes may be related to the structural distortions as in\textsuperscript{40} or from the compressive rGO forces, the significant changes are more likely to occur for electronic structure differences. Figure 3.10 shows the L-edge XANES spectra of bulk Fe\textsubscript{2}O\textsubscript{3} and a composite sample at normal illumination. The bulk Fe\textsubscript{2}O\textsubscript{3} spectra matches previously measured spectra for hematite.\textsuperscript{143} The most obvious difference is the massive difference in peak widths, especially in the lower energy L3 peak. The integrated area of the spectra correlates to the number of available states, such that a larger area indicates more holes. In this way, it is obvious that the bulk material has a significant amount more available states. In contrast, the composite shows many of it states are occupied. This indicates that the rGO transfers a significant amount of charge to the Fe\textsubscript{2}O\textsubscript{3}. This agrees with the XPS results shown previously. In addition, the pre-edge peak at \(~707\text{ eV}\) shows a large decrease as well. This is reminiscent of a reduction similar to magenmite (Fe\textsubscript{3}O\textsubscript{4}) or more accurately maghemite (\(\gamma\text{-Fe}_{2}O_{3}\)).\textsuperscript{143} This pre-edge feature is associated with Fe ions in octahedral sites, implying there is a fair amount of distortion that leads to the formation of tetrahedral Fe coordination in my samples. However, from the TEM, GIWAXS, and Raman, the crystal structure is definitely hematite. This should mean the changes are primarily due to surface restructuring possibly caused by the broken bonds at the surface. One last feature of note is there is a small, low energy shoulder that appears in the high energy L2 Peaks. This relates to Fe\textsuperscript{2+} states and is normally seen in the Fe\textsubscript{3}O\textsubscript{4} system. This makes sense as the measurements already show a significant change charge, but it highlights the degree of transfer. The amount of Fe\textsuperscript{2+} states available is not far from those available in the magnetite system. A similar feature should also be on the low energy edge of the L3 peak, but due to the lower quantity of states in this system and the much larger overall peak it is difficult to discern clearly. Simulations, as done with gZnO previously, or K-edge XANES/EXAFS results should give a better idea of the atomic structure and differentiate between electronic and structural contributions.

![Figure 3.10: XANES Spectra of bulk Fe\textsubscript{2}O\textsubscript{3} and composite rGO/Fe\textsubscript{2}O\textsubscript{3.}](image-url)
3.5 Magnetic properties of Fe$_2$O$_3$/rGO composites

As was mentioned previously, Fe$_2$O$_3$ is antiferromagnetic but displays ferromagnetism due to a canting of the magnetic moments leading to a net moment. Bulk crystals retain their ferromagnetism up to room temperature and down to ~ 260K where it experiences a Morin Transition and loses its magnetic moment. I wanted to determine if the composite structures of Fe$_2$O$_3$ exhibited any differences in the magnetic properties as a result of the various structural and electronic changes observed in the previous experimental work. One additional factor that is important is the size limit of ferromagnetism. The Mermin-Wagner theorem states that at very low thicknesses, thermal fluctuations have enough energy to randomly flip the magnetic moments of the atoms, making it impossible to exhibit ferromagnetism, instead becoming superparamagnetic.$^{144}$ My nanosheets are at the atomically thin level, implying this will become an issue. However, a few recent studies have shown that ferromagnetism is still possible at such low thicknesses in hematene and other materials.$^{40,137}$ As such, it is still worthwhile to check the magnetic behavior of the nanosheet composites and see if there are any differences that may stem from the rGO/Fe$_2$O$_3$ nanostructuring.

![Figure 3.11](image-url)

Figure 3.11: Magnetic SQUID measurements comparison between bulk Fe$_2$O$_3$ and a composite structure. a) MH curves for a bulk Fe$_2$O$_3$ film and a composite sample at 10K and 100K after subtraction of the linear antiferromagnetic component. b) A magnified version of the 10K plots in a) to highlight the ferromagnetism. C) MT curve of both bulk and composite samples under field cooled (FC) and zero field cooled (ZFC) conditions.

A thick composite and a thick film, made using the same amount of GO solution for the template, were measured using a SQUID, as shown in Figure 3.11. From the MH curves, the composite structure shows a near doubling of the coercivity from 700 Oer to 1100 Oer and magnetic saturation value from 0.00004 emu to 0.0001 emu, a small but not insignificant enhancement of the properties. The MT curves show the magnetism persists in both the film and composite structures, due to the high Neel and Curie temperature of hematite iron oxide. The negative values shown in the film are a result of a strong antiferromagnetic component and a low overall magnetic moment. Interestingly though, there is no observed Morin transition in either case. Previous work on hematite nanorods showed both an increase in coercivity and a decrease and eventual disappearance of the Morin temperature as well as a splitting of the zero-field-cooled and field-cooled T vs magnetization curve when the nanorods approached a size below 20 nm.$^{132}$ This also matches the behavior of the hematene. As such, the coercivity change appears to be from nanostructuring. However, the enhancement of the saturation value does not appear for hematene, indicating it is due to the composite interactions. The bulk crystal is still nanocrystalline such that it also does not have a Morin Temperature, but due to unrestrained growth and additional annealing the grain sizes are slightly larger leading to weaker properties. The strong splitting between the FC and ZFC curves indicates that the magnetic particles are not uniform in size, which is likely if we
assume the morphology of Fe₂O₃ is similar to that of the gZnO, and the moments get blocked at different temperatures. It appears that the size limitation did not manifest in this material. This is most likely due to some distortions either in the crystal structure, as is the case of the half unit cell Fe₂O₃ nanosheets, or in the magnetic structure.

In order to determine if the magnetic structure had changed significantly, we turn to X-ray Magnetic Circular Dichroism (XMCD) measurements. Essentially, XMCD differentiates between spin up and down electrons in XAS measurements. A more detailed description appears in Chapter B.2. Because XAS is sensitive to local geometry and electronic structure, it can be used to determine where the magnetic moments originate, both oxidation number and site, in the crystal. Figure 3.12 shows the XMCD spectra of bulk Fe₂O₃ and an rGO/Fe₂O₃ composite. Despite the very large change in the XAS spectra, there is very little change in the peak widths or peak intensity ratios and the magnitude difference most likely can be attributed to the lower percentage of Fe₂O₃ probed in the composite structure that leads to an overall lower signal that is difficult to process. The triple peak with opposite magnitudes is indicative of antiferromagnetic materials. Peak A corresponds to contributions from +2 Fe ions in octahedral sites, B is +3 Fe ions from tetrahedral components, and peak C corresponds to contributions from +3 Fe in octahedral sites. Despite having the formation of what appears to be Fe⁹⁺ states in the composite, the bulk Fe₂O₃ and composite have nearly identical ratios of the two peaks. This appears to indicate that either the Fe⁹⁺ states that form do not contribute significantly to the magnetic response or the electrons that have been transferred act nonlocally around the ions. The overall peak intensities are weak, and the data itself was difficult to obtain. Many scans showed charging and other effects that may be mitigated with better sample preparation.

![XMCD comparison of Fe₂O₃ samples. Composites were done at both 0.3 and 0.4 T while the bulk was only performed at 0.3T.](image)

Figure 3.12: XMCD comparison of Fe₂O₃ samples. Composites were done at both 0.3 and 0.4 T while the bulk was only performed at 0.3T.
The magnitude of the composite response is still much weaker than the Fe₃O₄ due to its crystal structure creating an isotropic dispersion of Fe²⁺.

In an attempt to maximize the strength of the magnetism, I attempted to form Fe₃O₄ inside the composite by heating the samples in a forming gas (4% H₂, 96% Ar) mixture. However, from side view images of the composite (Figure A.17), the iron oxide had formed large nanoparticles (~20-30 nm). In addition, Pt appears in the composite, instead of on top. This means significant damage had been done to the GO, creating voids in which the deposited platinum would fill. Graphene oxide can be annealed at much higher temperatures in hydrogen without damage, implying that this behavior appears to be due to a catalytic effect from iron that allows hydrogen to etch graphite by the formation of methane:¹⁴⁸⁻¹⁴⁹

\[ C(s) + 2H_2(g) \overset{Fe}{\rightarrow} CH_4 \] (3.2)
Chapter 4  Doping, alloying, and additional material nanosheet synthesis

gZnO, as grown by our methods, is difficult to characterize, particularly due to its insulating, wide band gap nature. This limits electronic and optic characterization. Chemical applications, such as hydrogen storage, are still possible, but is difficult to interpret and requires the use of composite structures specifically and specialized testing equipment. gZnO still remains an interesting direction, as dopants may show different incorporation and behavior in the graphitic structure and may facilitate the formation of 2D structures of other oxide structures. Additionally, gZnO can be functionalized through doping and alloying.

In addition, from the iron oxide synthesis, I can extend the functionality by choosing different materials that are more responsive to stimuli. This also helps set the boundaries on the utilization of this graphite oxide template method. I will discuss both of these directions in the following sections.

In section 4.1, I will discuss initial attempts at doping gZnO and possible directions. In section 4.2 I will discuss initial attempts at alloying. In section 4.3 I will discuss the synthesis of other oxides using the graphite oxide template method. In section 4.4 I will summarize the nanosheet growth and attempt to provide guidelines for the various behaviors. In section 4.5 I will summarize intercalation efficiencies of several materials and potential reasons for the differences.

4.1 Doping

Currently, there are many limitations to using single gZnO nanosheets. The naturally insulating behavior, wide band gap, polycrystallinity, and possible interactions with the substrate have made it difficult to determine any electrical transport properties. The wide bandgap itself poses a problem, as it can only absorb or emit light only at relatively deep UV frequencies, a relatively uncommon range. In the composite form, there are more possibilities. However, some measurements, such as optical transmission, are difficult due to the domination of GO and a low concentration in the composite. Other methods may be more promising, such as chemical experiments, such as for catalysis or gas adsorption, in which the chemical only reacts with the gZnO. However, these methods are outside the capabilities of our lab. Instead we turn to discovering how to functionalize gZnO.

The easiest way to functionalize materials is through the use of dopants. The most common dopant for ZnO is aluminum, and it can greatly increase the conductivity of ZnO. Additionally, some theoretical studies show promise for Al:gZnO as a catalyst for CO oxidation. This is the first element other than ZnO we tested for this growth procedure, and actually was grown before pure ZnO. Figure 4.1 shows an AFM image of sub-nm Al:gZnO step with a second sub-nm step. From the EDX scans of composites on holey carbon TEM grids, Figure 4.2, it is very clear than aluminum incorporates into the GO quite well and shows no clear evidence of clustering. XPS scans were also performed (Figure 4.3). The aluminum spectra show a full +3 aluminum oxidation state, instead of any aluminum metal or complex formations, for both bulk and composite samples. This does tend to support the formation of dopants, especially considering the low Al concentration (~1%) but cannot rule out the formation of alumina. Ideally, HRSTEM imaging of a monolayer or bilayer structure would be most definitive, although X-ray diffraction may be sufficient. The spectra also show a decrease in the binding energy in Al in the composite. This appears to indicate
that the graphite might compensate some of the charge lost by Al in the gZnO matrix. It is unknown what effect this may have for doping. Ultimately, further electron transport measurements have yielded no results so far, but this experience shows that doping is compatible with this method.

Figure 4.1: AFM imaging of AZO nanosheets. a) Optical image of an AZO/rGO composite on SiO$_2$/Si. B) AFM image of the white boxed area in a) after calcination. c) Linescan along the white line in c) showing roughly a bilayer thickness.

Figure 4.2: EDX dispersion of AZO. Elements are labeled in the figures.
Transition metal doped ZnO (TM:ZnO) has been studied in the past as a dilute magnetic semiconductor. Nearly every type of magnetism from TM:ZnO have been reported, including ferromagnetism, weak ferromagnetism, paramagnetism, superparamagnetism, and antiferromagnetism. In fact, Fe:ZnO alone has exhibited all of these magnetic properties. Most reports show ferromagnetism at or above room temperature, although a few also show transitions from paramagnetism to ferromagnetism as the temperature decreases. Additionally, the strength of the magnetism can increase significantly as the temperature decreases.

There is some debate on what the true cause of the magnetic response. Some reports point to the dopants causing magnetization of the entire material, while others claim small complexes of iron or iron oxide, too small to detect using conventional XRD, contribute to the overall magnetic field. An additional concern is the size limitation of magnetism, as previously discussed with the Fe₂O₃ nanosheets. However, the theoretical papers on transition metal doped gZnO mentioned earlier seem to imply these doped nanosheets will retain ferromagnetism, or antiferromagnetism. In either case, I wanted to observe a magnetic response from Fe doped gZnO.

Fe:ZnO tends to have weak ferromagnetic properties, so it is also difficult to test for ferromagnetism in single sheets. As a result, the experiments started with using composite structures that have a large majority of gZnO samples. It is not possible to separate out the contributions from Fe:wZnO bulk pieces that are in the composite and contributions from gZnO, but it should either significantly smaller.

I first started with XPS to determine the oxidation state of the Fe. Most papers report iron doping as Fe(II), which exhibits a much lower binding energy in XPS spectra, although Fe(III) and a combination of both are sometimes observed. Additionally, ferromagnetism has been found with mainly +3 considerations, indicating the oxidation state is not critical. From our XPS measurements, the major Fe peak for bulk Fe:ZnO is near the Fe 3+ peak at 710.8 eV. This can also be verified by the satellite peak that appears at around 718 eV. Fe energies of the composite shows a 0.8 eV increase in the binding energy relative to a bulk Fe:ZnO film. This occurs for all concentrations tested, from about 4% to about 15% Fe. This increase is unusual, as it appears to
contradict the behavior of pure Fe$_2$O$_3$ composites and may point towards a strong interaction with the gZnO.

![Graph showing XPS measurements of the Fe 2p peak in Fe:ZnO samples.](image)

**Figure 4.4**: XPS measurements of the Fe 2p peak in Fe:ZnO samples.

![GIWAXS images for different concentrations.](image)

**Figure 4.5**: Fe:ZnO GIWAXS for different concentrations.  
a) High concentration (~26% Fe) bulk film showing unusual scattering structure as a result of the high concentration of Fe.  
b) Low concentration (<5%) bulk film showing only ZnO diffraction.  
c) Thin composite film of the high concentration of Fe showing a slight Fe$_2$O$_3$ feature.  
d) Thin composite film of the low concentration sample showing no Fe$_2$O$_3$ signal.
There were no observed differences in the solubility of Fe between gZnO or wZnO using GIWAXS. However, this technique still allows us to distinguish between Fe:ZnO and an FeZnO alloy. From the GIWAXS measurements (Figure 4.5), higher concentrations Fe was incorporated in ZnO. In the tested samples, higher concentrations showed phase separation (~26% Fe measured) while low concentrations did not (<5%). This also confirms the XANES spectra on Fe:ZnO samples presented later were indeed doped samples. There is one unusual feature, however. Even in the thin composite case, there is strong out of plane scattering. This may be due to some growth instabilities due to the Fe incorporation. However, there is also a strong powder diffraction ring near 3 Å⁻¹ that most likely corresponds to rGO. This may indicate why there appears to be significant powder ring contributions from various diffraction directions, but it does not explain the large out of plane component. It is possible the rGO is highly wrinkled, creating voids in which larger crystals can form, contributing to out of plane contributions. Regardless, Fe₂O₃ diffraction is not visible, so it can be implied that there is no phase separation. This may not be perfect, as the low diffraction intensities makes it difficult to guarantee no formation, but it is a good starting position.

XANES spectra for bulk Fe₂O₃ and composite Fe:ZnO of various concentrations are presented in Figure 4.6. Previous XANES results on Fe:ZnO nanoparticles show a spectra that closely matches bulk Fe₂O₃ and has a predominantly +3 XPS contribution. In contrast and despite the large +3 contribution in our XPS results, our spectra does not appear to significantly match the bulk Fe₂O₃ contribution. The spectra show markedly narrowed peaks, similar to Fe₂O₃, which seems to contradict the XPS results. A rising binding energy typically denotes a loss of electrons, increasing the number of available states and widening the XANES spectra. Once again, this is most likely due to interactions with ZnO. There are other features of note, one of which is indicated by the arrow in Figure 4.6, which has significantly decreased in the Fe:ZnO composite case. The feature near 718 eV that was relatively strong in the composite Fe₂O₃ case is not visible in the Fe:ZnO spectra. Additionally, as the Fe concentration dips, the pre-edge feature weakens until it is a weak shoulder. This is even closer to the Fe₃O₄ spectra. While this may indicate a change in the local geometry of some of the Fe (Fe₃O₄ has half tetrahedral contributions), it may still simply be changes in the electronic structure similar to observations from the Fe₂O₃ composite. K-edge analysis may offer a better option for separating electronic and structural features. The peak energy of Fe:ZnO composites is also slightly larger than that of Fe₂O₃, although it is at the limit of the resolution for this technique. It should be noted that the concentrations listed in the graph are unusually high, greatly above the solubility of Fe in ZnO. However, this is because the concentration of Fe in the composite is very low, usually only a few atomic percent of the total system. This makes it very difficult to pick up in the composite form, both for XPS and XANES. In XANES, it can make it impossible to discern the fine features of the spectra. In XPS, the peaks can be near noise level, making estimation of the concentration difficult. As such, the Fe percentages are most likely lower than the reported values in the graph. As such, the data should be a guide and be interpreted with these details in mind.
Figure 4.6: XANES spectra of bulk Fe$_2$O$_3$ and Fe:ZnO composite structures with different Fe%. The black arrow indicates a strongly weakened feature.

The XAS spectra were quite strong, and I attempted to perform XMCD similar to the Fe$_2$O$_3$ case. However, the XAS samples were still comparatively weak and excess charging caused the spectra to become distorted and ultimately unreliable. Additionally, initial SQUID measurements also showed no discernible magnetic moment, either due to the very weak nature of the DMSC or because of a lack of magnetism in the samples. As such, it is currently unknown if Fe:ZnO has any magnetic properties, and requires further investigation. Additionally, Co may also be a better alternative due to showing ferromagnetism in ZnO nanoparticles.$^{154}$

4.2 Alloying

Another direction of interest is alloying other materials with gZnO. ZnO has often been alloyed with MgO, to increase the bandgap, and CdO, to decrease the bandgap. Both of these materials crystallize in the rocksalt structure. It was predicted that this crystal structure could also form a low energy graphitic structure at very low thicknesses for its 111 surface.$^{50}$ Reports on this structural change have been inconclusive so far, due primarily to inconsistencies in synthesis. If ZnO alloys with CdO or MgO, it may be possible for ZnO to stabilize small crystals of MgO or CdO. For example, MgZnO remains in the wurzite phase up to 4% MgO before phase separation, although it may be higher due to a metastable configuration.$^{155}$ It may be possible, near this point,
to observe graphitic MgO intermixed with gZnO. Alternatively, if MgO can demonstrate a graphitic phase, it may be able to alloy with ZnO through the entire composition range instead of undergoing phase separation. Facile alloying would further enhance the parameter space offered by this new phase of ZnO.

CdO is more toxic than MgO, so we opted to start with MgO first. MgO has a lattice parameter of 4.212 Å. Figure 4.7 shows a sub-nm MgZnO sample. The clear layering pattern is almost identical to ZnO, implying MgO or MgZnO has sub-nm layering in the composite like gZnO. From a FIB sample, Figure 4.8, we see that there is no obvious agglomeration of MgO and we still observe the planar shape growth of gZnO. Most importantly, however, is the interface layer. From the EDX linescan, Figure 4.8b, we see a slight peak of both Mg and Zn at the interface, indicating the Mg and Zn are occupying the same sub-nm layer. This means that Mg is indeed in a sub-nm form, either as sub-nm MgO or as MgZnO.

Figure 4.7: AFM of a MgZnO nanosheet. a) Optical image of a MgZnO/rGO composite. b) AFM image of the MgZnO sheet in the red boxed area in a) after calcination. c) Linescan corresponding to the white dotted line in b).
Figure 4.8: Side view image of a MgZnO composite. A) STEM-HAADF image of a side view MgZnO sample and corresponding elemental maps. b) Integrated EDX linescan of the red boxed region. The black arrow indicates the position of a peak that corresponds to the interface layer, showing that both Mg and Zn are in the interface layer.

I attempted to perform GIWAXS scans on composites and nanosheet MgZnO. Unfortunately, two issues occurred. First, in composite samples (Figure 4.9), the lower crystalline quality of the alloys caused the nearby GO peak and the MO peak to become indistinguishable, unlike the pure MgO shown in Chapter 4.3. This makes it difficult to analyze truly alloyed MgZnO. Additionally, from GIWAXS measurements on pure MgO nanosheets, and follow up work with NiO, the Mg incorporation in the surface layer is much lower than ZnO. It is very difficult to determine the concentration of MgO in the gZnO layer. Even very high Mg concentration MgZnO sheets only show ZnO diffraction, putting in question the concentration in the surface layer. However, it does allow us to perform a few more measurements to learn about pure MgO.

Figure 4.9: High Mg Concentration MgZnO nanosheet composite GIWAXS scan.

In order to follow up this work, transfer of single gMgZnO nanosheets would be preferable, as this would be able to more clearly distinguish between MgO and ZnO without the interference from the rGO.
Figure 4.10: XANES of MgZnO nanosheets.

Figure 4.10 compares the XANES spectra of bulk MgO and MgZnO nanosheets. As was mentioned previously, MgO has a low solubility and the MgZnO sample presented here had a relatively high (~20%) Mg concentration, so the Mg XAS spectra most likely gives the spectra for ultrathin MgO. This can be corroborated with the double peak formation in the ultrathin samples that matches similar trends in ultrathin films of MgO.\textsuperscript{156} As the thickness of the MgO film decreases, the low energy peak intensity strongly decreases. My MgO low energy peak has become a shoulder, due to a reduction of the average number of scatterers, indicating that our samples are even thinner than 3 monolayers. Additionally, the two higher energy peaks have merged together, another indicator of the ultrathin nature. There is a slight shift of the higher energy peak to lower energies, not seen in the reference literature. This may be a result of interactions with ZnO or with the substrate. Ultimately, the changes in the XANES structure are very slight overall. This may indicate that the MgO does not undergo a structural change other than possible distortions due to the nearby ZnO or from the ultrathin nature. These films also are 002 oriented, which is not the expected direction for a graphitic transformation.\textsuperscript{157} Even in the presence of ZnO, graphitic MgO does not occur. However, MgO monolayers are possible with this method.

4.3 Other oxides

So far, I have demonstrated that this synthesis can be used for at least two oxide materials. It would, at this point, be wise to consider what the limitations may be to this technique. The first limitation is immediately obvious: its usage for non-oxide materials. The reduction of GO causes a highly oxidizing atmosphere, making non-oxide synthesis incredibly difficult. However, for oxide materials, the limitations are not as obvious. Therefore, it would be worthwhile investigating this further. A straightforward method for this is to attempt to synthesize different types of oxides. Since there are many options available, it is wise to select a few different systems that 1) have potentially interesting properties and/or 2) have some structural difference to see if it behaves differently from previously attempted samples. My initial choices were MgO, NiO, CuO, and Al\textsubscript{2}O\textsubscript{3}. My reasoning for these materials is as follows:
Magnesium oxide was discussed previously in the alloy section. It is an obvious choice, as I needed reference samples for comparing with the gMgZnO alloys. Rocksalt is also one of the potential structural change materials mentioned in literature (Figure 4.11).

Nickel oxide is an interesting material, as it is a p-type wide band gap oxide that has been studied to make transparent electronic devices.\textsuperscript{160} Many oxides are naturally n-type doped, such as ZnO and SnO\textsubscript{2}, and it is difficult to create p-type forms. Additionally, other oxides that are p-type tend to be not fully oxidized, such as SnO and CuO\textsubscript{x}, which makes them less stable. It crystallizes in the rocksalt structure.

Aluminum oxide, similar to MgO, was used as a dopant and was synthesized to potentially compare as a reference case. However, alumina works well as a dielectric media, generally providing higher gating efficiency than SiO\textsubscript{2} and could be used as an oxidation resistant replacement for BN.\textsuperscript{161} It crystallizes in the same structure as hematite.

CuO is an interesting material in particular as many high Tc superconductors believe some form of copper oxide layer (Cu\textsubscript{2}O, CuO, or CuO\textsubscript{2}) is responsible for the superconducting properties.\textsuperscript{162} It is also a low band gap (~1.2 eV) p-type semiconductor.\textsuperscript{163} It crystallizes in a monoclinic structure (Figure 4.11).

4.3.1 MgO

I first attempted MgO since it was previously studied as an alloying element. From the AFM images, MgO does appear to form monolayer or bilayer sheets. However, it does not retain the same thickness relation as ZnO. It requires much more GO to obtain the same gZnO thickness. MgO also incorporates into GO at a much lower percentage than ZnO, making diffraction and other measurements quite difficult. Additionally, thinner sheets do not form a sharp edge. The
bottom edge of the sample in Figure 4.12b has a sharp edge while the top edge shows a significant roughness and an overall porous morphology. The porous nature and general noise make it difficult to determine if a monolayer has actually been achieved, but bilayers show a significantly sharp edge, as seen by the 4.2 Å step seen in Figure 4.12c.

Figure 4.12: AFM images of a MgO nanosheet. a) Optical image of a MgO/rGO composite before calcination. b) AFM image of the boxed area in a) after calcination. c) Linescan of the dotted line in b).

Figure 4.13 shows a composite sample and an NBED diffraction pattern from the composite. There is a hexagonal pattern corresponding to rGO and a square pattern from the MgO, indicating that the MgO samples are oriented in the 002 direction and not the 111. The single diffraction pattern is unusual for such a thick piece. It seems that for this particular case, it is unlikely this diffraction pattern is from a thin MgO sample. The diffraction patterns only occur in certain areas on certain samples, making it seem as though a larger crystal is necessary to produce enough diffraction to detect. If a sheet is thin enough, it is possible to hit only one grain. Since each layer has different gaps where ZnO crystals do not lie, it is possible to hit only one grain. The chance of this is very low, as can be seen from the filling of our FIB samples of ZnO, and once again, there was never an instance of more than one diffraction pattern from the MgO. However, this does prove that the conditions we use can produce crystalline MgO, indicating it is highly likely MgO can crystallize within the layers.

Figure 4.13: TEM Characterization of MgO. a) HAADF-STEM image of a composite structure. B) NBED Diffraction image of the composite shown in a). Red boxes indicate diffraction from MgO. The last spot is under the beam stop.
GIWAXS provides a much more enlightening view. Figure 4.14 shows GIWAXS scatter plots of a thick MgO film and a MgO composite structure. Thin composites and nanosheets produced no diffraction, most likely due to the unusual filling behavior observed from the AFM images. The bulk film shows a strong powder profile while the composite structure shows only 002 in plane diffraction, a strong indicator of texturing and thin nanosheets. As mentioned previously mentioned from the NBED images, the GIWAXS show clearly that the MgO does not form along the 111 direction, making it unlikely that a graphitic structure formed. However, it is very likely sub-nm nanosheets of MgO textured in the 002 direction have been synthesized. Figure 4.15 shows the radially integrated plot of the GIWAXS data. The composite shows a two peak structure, with the lower Q (2.95 Å⁻¹) peak belonging to GO and the larger Q peak (3.05 Å⁻¹) belonging to MgO. The bulk film has an unusual higher Q peak on top of the broader peak that more closely matches the MgO literature values, and is most likely an additional peak arising from multiple scattering effects. As such, it appears that the MgO lattice spacing decreases slightly, indicating an in-plane compression. This is markedly different from the behavior of the Fe₂O₃. This may be due to the smaller MgO intercalation which can lead to a ravioli-like wrapping of the two GO sheets around the MgO.

![GIWAXS scatter plots of MgO samples. a) Bulk MgO. b) Composite.](image)

Figure 4.14: GIWAXS scatter plots of MgO samples. a) Bulk MgO. b) Composite.
4.3.2 NiO

The low Z-contrast relative to GO also makes the side view imaging of FIB samples difficult. The extremely high bandgap of MgO makes electronic characterization difficult as well. In order to more easily study the rocksalt family, NiO was synthesized instead. Figure 4.19 shows AFM images of NiO nanosheets that show a thickness of around 4.25 Å, which corresponds roughly to a unit cell ($a_{\text{NiO}} = 4.179$ Å). This would imply that the nanosheet is oriented along the 001 direction. From GIWAXS data, Figure 4.17, it is clear that NiO samples are grown oriented along the 002 direction, similar to MgO. Due to the unusual peak shape (Figure 4.18), it is difficult to determine if the nanosheets have any shifts in the peaks.

Figure 4.15: Radially integrated plots of the GIWAXS scatter plots for a MgO composite and bulk film.
Figure 4.16: NiO Nanosheet AFM Images. a) Optical image of the NiO/rGO composite. b) AFM image of the NiO nanosheet after calcination. c) Linescan of the white dotted line in b).

FIB lamella, Figure 4.19, were fabricated to see if NiO forms an interface similar to Fe$_2$O$_3$ and ZnO. However, no interface layer was visible, although it was clear that the NiO does grow in an elongated fashion, so the GO still has an effect. The elongated crystals also seem very thick, which is unusual given the AFM images.
Figure 4.17: GIWAXS scans of NiO samples. a) Bulk NiO. B) Composite NiO/rGO.
Given this morphology, it may explain why MgO exhibits the unusual AFM pattern shown in Figure 4.12, and shows that the two rocksalt structures show very similar intercalation behavior. Essentially, unlike ZnO and Fe₂O₃ that form an interface layer, NiO and MgO only exists in between layers. This means there is no base to form a clean complete ultrathin layer, and instead, require a thick composite such that smaller sheets sinter together to form a porous, but continuous nanosheet. In this way, sub-nm NiO and MgO are being formed, but in a morphology that differs
significantly than ZnO and Fe₂O₃. The changes are very small comparatively such that AFM has a hard time distinguishing the changes.

4.3.3 CuO and Al₂O₃: Nanoparticle formation

Two materials I studied showed no nanosheet formation: CuO and Al₂O₃. CuO and Al₂O₃ both form nanoparticles under normal conditions, as can be seen from the AFM images in Figure 4.20 (Al₂O₃ is shown in Figure A.18). Even in the composite form, Figure 4.21, with the rGO still applying a compressive force, the CuO still shows nanoparticle formation. This shows that due to the flexibility of GO, it cannot act as a perfect inhibitor of out-of-plane growth. It may be worthwhile to mention that lower temperatures might prevent some of the coarsening behavior and may be an interesting avenue of study.

Figure 4.20: Formation of Copper Oxide Nanoparticles. a) Composite structure before burning carbon away. B) AFM scan after calcination of area boxed in red. c) Linescan along white line in b).
4.4 Discussion of appropriate crystal structures

From the above observations, there appears to be three regimes. First are materials that form a uniform interface layer and exhibit two dimensional nanosheets. Second are materials that can be synthesized in a two-dimensional fashion, but do not form a uniform layer at the surface of the substrate. Third are materials that do not exhibit 2D nanosheet growth using this method.

ZnO and Fe$_2$O$_3$ create the most complete nanosheets, with an interface layer and well-defined step heights. However, they do not show very many similarities. Both have different crystal structures, oxidation states, band structures, and electronegativities. As such, it may be more prudent to start with materials that do not form the interface layer in order to shed some light onto what the important properties are.

Both materials that exhibited planar structures but no interface layer are MgO and NiO. Both of these materials exhibit a rock salt structure. Other than that, they do not share very many similarities. Rocksalt is a nonpolar system in which the anions and cations reside in the same plane. Conversely, both ZnO and Fe$_2$O$_3$ in their bulk forms have the O and cation displaced from each
other in the z direction. This out of plane component of the bonding may help attract and bind the precursors to the SiO$_2$ surface.

So far, the only two materials that were not able to create nanosheets are Al$_2$O$_3$ and CuO. CuO forms in a monoclinic crystal structure while Al$_2$O$_3$ has the same structure as hematite, with oxygen ions forming a hexagonal close-packed structure with the aluminum ions filling two-thirds of the octahedral sites. As such, it appears as though materials with reduced symmetry crystal structures are less likely to form clean nanosheets through this method. This is obviously not the full story, as Fe$_2$O$_3$ also has a trigonal structure. In fact, it has a very similar crystal structure with the cation filling two thirds of octahedral sites of an oxygen HCP structure. However, here electronegativity and charge localization may play a role. Al$_2$O$_3$ forms much stronger ionic bonds that may not be as amenable as the bonding in Fe$_2$O$_3$. A more thorough investigation is warranted, however, and theoretical work on potential nanosheet forms of CuO and Al$_2$O$_3$ could provide much greater insight.

### 4.5 Discussion of intercalation efficiencies

Many different elements have been used for intercalation in this project, including Zn, Mg, Fe, Ni, and Al. Through the studies, I found that each element has a very different intercalation efficiency. For example, Al incorporates very readily, much higher than any other element. On the other hand, Mg intercalates with a much lower efficiency, only about 10% that of Zn. Interestingly, the pattern for elements that intercalate efficiently versus those that do not has been difficult to determine. A comparison of efficiencies is presented in A.7. At first it was thought to be the size of the ion, as Al incorporates very easily. However, Mg does not incorporate very efficiently and has an ionic size similar to that of Al and a much smaller size than Fe or Zn. I then thought it was related to the precursor attachment. However, Al is a nitrate, as is Fe, and they have drastically different efficiencies. Zn and Mg are both acetates, but Mg incorporates with much lower efficiency than Zn. It was then theorized it was the amount of hydrates attached to the precursor. However, Fe and Al both have 9 attached and have very different efficiencies. For comparison, Mg has 4 and Zn has 2. Currently, I believe it may be a combination of factors. Al with 9 attached hydrates may be preferentially incorporated with GO’s hydrophilicity. This combined with a smaller ionic size may account for the large difference. However, further studies would be necessary to confirm this hypothesis.
Chapter 5  Conclusions and future work

5.1 Conclusion

2D materials are coming to the forefront of advanced technologies. Both van der Waals materials and non-layered nanosheets require significant development before reaching widespread application. For non-layered oxides, synthesis remains a significant hurdle. However, nanostructuring provides a wealth of advantages, usually in the form of higher activity and surface area, which can be further enhanced by mixing with graphene or rGO. Already, nanostructured composites have shown enhanced photocatalytic properties, higher energy capacity in batteries, and stronger sensitivity in chemical sensors. g\text{ZnO}, and other layer-dependent structure materials, provide an interesting opportunity for bridging the gap between 2D and 3D materials combining features from both realms for both composites and nanosheets. These materials have been experimentally limited due to the difficulty in fabricating it easily and in large quantities. This new method of synthesizing nanosheets is very attractive due to the advantages of rGO and the ability to perform the synthesis with multiple materials.

It was found that the GO template method utilizing aqueous precursors and high temperature annealing could fabricate monolayer g\text{ZnO} in addition to bilayer and trilayer samples that show sizes up to 50 \mu m. The technique can also be modified by using oxygen plasma instead of a high temperature calcination. g\text{ZnO} was shown to have a massive increase in the bandgap, up to 4.8 eV or higher, based on XAS, XPS and EELS. The band structure also significantly changes, with a large increase in the availability of the 4s states. The pre-edge feature seen in XANES spectra has been correlated to broken symmetry at surfaces that results in a planar surface, although attachments and substrate interactions can create similar effects. Because the ultrathin nature of my samples exemplifies primarily surface components, the pre-edge feature can act as a fingerprint for the g\text{ZnO}. GIWAXS measurements confirm an expansion of the lattice as well, and confirms the interface layer is crystalline. This g\text{ZnO} is also stable at high temperatures, up to 800°C, that makes it suitable for high temperature 2D applications, unlike bulk w\text{ZnO} and conventional 2D materials. The transport measurements show relatively weak properties, most likely due to extrinsic effects from the substrate and other defects but is relatively unique since almost no literature of nanosheet synthesis of non-layered materials (at least for the bulk crystal) have measured transport of single sheets.

This technique was found to extend to \textasciitilde 0.6 nm Fe\textsubscript{2}O\textsubscript{3} nanosheets. These nanosheets show significant expansion in the composite structure as determined by GIWAXS and hinted at by Raman shift measurements. The composites show enhanced UV absorption when compared with rGO as well as enhanced coercivity and saturation values when compared to bulk Fe\textsubscript{2}O\textsubscript{3}, although XMCD results show no change in the magnetic structure. The XANES results show a massive decrease in available states and hints at a composite structure that somewhat resembles Fe\textsubscript{3}O\textsubscript{4} including the formation of Fe\textsuperscript{2+} states, but the electronic and structural components of the spectra have not yet been separated. XANES also points to a high percentage of tetrahedrally coordinated Fe, most likely due to surface reconstruction.

Additionally, there is some evidence that NiO and MgO nanosheets can also be fabricated with this method, but CuO and Al\textsubscript{2}O\textsubscript{3} cannot. The composites of all these materials show significant changes in the electronic structure as determined by XPS.
Side view imaging of gZnO and Fe$_2$O$_3$ have shown the formation of a complete, clean, and long-range interface layer that forms the base of the nanosheets and prevents observation of porosity in samples using AFM. Above the interface, the sheets are partial, forming islands only a few nm across. These are specimens that can be considered freestanding due to the weak van der Waals interactions with the graphene. This also explains the porosity in freestanding samples fabricated over a hole. NiO and MgO do not show an interface layer, but do show very thin samples between rGO sheets. Al$_2$O$_3$ and CuO show only nanoparticle formation. These differences are attributed to differences in symmetry and high energy surfaces.

This method facilitates easy doping (Al, Fe into ZnO) and alloying (MgZnO). Fe shows doping behavior from GIWAXS measurements, while MgZnO is still undetermined. The dopant and alloyed elements show significant changes due to both rGO and ZnO.

These nanosheets and composites show significant promise. Theoretical results point to everything from piezoelectricity and enhanced photocatalytic properties, in addition to simpler applications in composites for batteries, energy production, and more. As such, this synthesis method provides a first step in a highly exciting direction.

5.2 Looking forward

Several straightforward future studies were mentioned in Chapter 4, involving the functionalization of gZnO. Primarily this involves the use of dopants to impart properties to the ZnO, such as transition metals for magnetism or Al for better conductivity. There are also improvements that need to be made to the electronic properties through various means, including reducing substrate interactions. These are very material specific, and there is a significant amount of work that can be done in the process.

The first major follow-up study to this work is to find a way to increase the intercalation efficiency between GO layers. Currently, the synthesis method for large area samples does not differentiate itself much from thin film deposition techniques since it requires the SiO$_2$ substrate for large nanosheets. Although small nanocrystals of gZnO can be made, they are not as useful as the large area nanosheets. Large nanosheets in between gZnO would enable true large area, freestanding gZnO that could be placed on arbitrary substrates/gaps and further studied by microscopy. The increased efficiency would also allow gZnO signal to be picked up stronger, potentially opening up more optoelectronic studies. It is possible a hydrothermal or electrochemical method may aid this direction.

The second major follow up would be to create single crystal nanosheets instead of polycrystals. Many studies, especially with 2D materials, rely on their single crystal nature to obtain results. Some are very advanced techniques, ARPES (Angle resolved photoemission spectroscopy) can obtain the full electronic structure of 2D materials and can provide wealth of information about the optoelectronic properties. However, the angle can only be interpreted correctly for single crystals with grain sizes above approximately 200 nm. Some are simpler, such as being able to perform incredibly high-resolution side view imaging. Polycrystalline materials are difficult to align and image due to the random orientation. In plane piezoelectricity is also impossible to study, as the random displacement of the individual grains will cause a negligible net displacement. There are also practical reasons why polycrystalline materials are more difficult to study. Grain boundaries act as defects. In this way, many optoelectronic properties are diminished, making studies such as Raman and transport measurements more difficult. They also act as weak points in the material. Under electron beams, it is very likely the material would break.
down due to the structural weakness from grain boundaries. Additionally, many ways to identify monolayers in the TEM requires a single crystal such that diffraction patterns can be compared at different tilts. Both of these two directions require a fundamental knowledge of the process, including how the interface process develops and the mode of precursor transport. Once again, a hydrothermal or electrochemical approach may show improvements.

Moving forward, this method of synthesis may be extended to other oxide materials and help realize the 2D phases of a large variety of conventional materials, some of which have already been predicted. Currently, this technique is limited to oxides due to the relatively high oxygen atmosphere due to the reducing GO. However, the use of the gaps in GO could be used for more general nanosheet synthesis. A low temperature process combined with the hydrogen plasma-based removal could utilize the GO without creating significant oxidation conditions. Alternatively, intercalation could be performed with the cation and anion and the GO could be reduced chemically before heating. This could further improve the parameter space of non-layered nanosheets. Other methods could be used, such as selenization or sulfurization to replace the anions.

Additionally, using synchrotron radiation for the structural verification of gZnO is inconvenient and time consuming, and a faster approach should be found. Typically, 2D materials utilize shifts in the Raman spectrum to determine monolayer. gZnO has an entire structural change, but unfortunately does not appear to be Raman active in its current form. If a similar measurement could be discovered, identification and study of gZnO would greatly benefit. Likewise, studying wide-band gap 2D nanosheets remains a challenge, as typical characterization techniques like photoluminescence cannot be used due to a very wide bandgap. Combined with a low conductivity, this greatly reduces the usefulness of gZnO and greatly inhibits study. This does not prohibit chemical or dielectric functionalities, but it brings gZnO outside the realm of classic ZnO study.

Finally, gZnO heterostructures can be open up a variety of directions. gZnO is very similar to hBN and may have some similarly interesting work. hBN has been used for many interesting studies with graphene and other 2D materials, including tunneling physics, hyperbolic metamaterials, and ultrahigh mobilities. gZnO has a much stronger ionic component and may modify these applications in unique ways as well as potentially enabling new physics. This would require extensive theoretical probing, as first principles calculations would be needed to accurately probe the strong interactions between single or bilayer gZnO and graphene or other 2D materials.
Appendix A Additional figures and data

A.1 Exfoliation of thin films

Figure A.1: Composite films after a “blow-off.” a) A high magnification SEM image of the composite structure after blow off. b) A low magnification SEM image of the composite structure after blow off showing the relative uniformity. c) AFM image of the composite showing a majority of 1-3 layer GO structures. d) Image showing the chip after the blow off. A and B indicate complete blow off while C shows a partial sample. e) High magnification SEM image of the nanosheet dispersion created by the thin composite film in a). f) Low magnification SEM image of the nanosheet dispersion showing uniformity over large scales.

Up to this point, this phenomenon of a thin GO film was only visible after a thicker film has been blown off, as seen in Figure A.1. This process is hard to reproduce, although it is made easier by a few observations. This does not work for thinner GO films. Additionally, it works better for films that dry very uniformly from the edge of the droplet towards the center. These two observations lead me to hypothesize that the reason these films will blow off is due to gas buildup during heating. The film, when dried very uniformly, creates a seal that slows the escape of gases. Excess water vapor and released O₂ from the reduction of GO causes a gas buildup within the film. When a certain pressure is reached, the top layers of the composite blows off, leaving behind a semi-uniform thin film of GO. The reason the bottom layers stick better to the substrate is most likely due to 2 factors. First, the ZnO layer on the SiOₓ most likely sticks better to the substrate and allows the first few layers of GO to stick as well. Second, the bottom layer is usually free of any wrinkles or voids caused by random stacking of GO. These sites are where gas will collect originally, and also areas of weaker sticking. This means only the top layers will dislodge. In any case, this process is still difficult to control. Making sure the GO films are sufficiently thick helps, but many times the film will not blow off. One option is to use tape to exfoliate the bulk of the
film, as seen in Figure A.2. However, since it did not blow off on its own, certain areas are more firmly attached and show thicker regions and a higher concentration of GO thicker than 3 layers. However, areas hundreds of microns in size are still attainable. Instead, we wanted to find a method to create an initial very thin and uniform GO film.

GO sheets dry naturally in a coffee ring pattern, as seen in Figure A.3. This is caused by the hydrophilicity of GO. The GO likes to stay in the water droplet for as long as possible, so most of the sheets will prefer to stay in the droplet until it shrinks down to a very small size and the sheets form a very small film in a concentrated area. Since the behavior of GO is determined by hydrophilicity, it makes sense that the substrate should be hydrophilic in order to spread the water and cause the GO to stick more preferentially. Unfortunately, many hydrophilic materials are polymers. Luckily, it is possible to treat the surface of SiO$_2$ to become more hydrophilic. PDMS, when treated with an O$_2$ plasma, becomes more chemically active and can bind better to glass and other samples. It turns out, this same principle helps SiO$_x$ become more hydrophilic. Optical images, Figure A.3, also confirm the spread of the GO. This method is still not perfect, as the coffee ring pattern can still be visible. However, it is slightly more controllable than the thick GO film and uses much less GO.

Figure A.2: Using tape to peel off excess GO. a) Image showing the tape has removed top portions of a composite, leaving behind a thin layer on the Si wafer, which is invisible to the naked eye. B) AFM and c) SEM image of the area removed by tape. D) Optical microscope image of a similar sample on SiO$_2$/Si. This shows both the thick areas that are not removed as well as a thin sheet dispersion.
Figure A.3: O₂ treatment comparison to normal drying conditions of GO. a) High density coffee ring pattern of GO. b) Low density coffee ring pattern of GO. C) Example dispersion of an O₂ plasma treated substrate. D) Higher magnification image highlighting the few-layer contrast of the dispersion.
A.2 GO height vs final ZnO thickness comparison

Figure A.4: Comparison of composite height vs nanosheet height.

Figure A.4 shows how the height differs between the composite and the sub-nm gZnO sheet. B) shows the composite height of about 2 nm, which corresponds roughly to 3-4 layers of GO. It is difficult to say specifically due to the ZnO in between the sheets. After burning, only a 0.5 nm ZnO sheet remains, which corresponds to 2 layers. This reconfirms the idea that each gap is only partially filled with ZnO.
A.3 Additional ZnO NBED

Figure A.5: NBED Diffraction images from “pure ZnO Nanosheets.” Figure A.5 shows multiple diffraction spots from a “nanosheet” suspended over a holy SiO₂ grid. This shows significant out of plane diffraction, such that it is likely bulk crystals are also formed.

Figure A.6: NBED Diffraction image from a multisheet composite structure. a) HAADF of a composite with multiple GO sheets stacked on top of each other. B) Corresponding NBED diffraction image.

Figure A.6 shows an HAADF image of a multisheet composite structure and the corresponding NBED pattern. As seen, the rGO now shows rings, confirming many different rGO sheets, and diffraction from ZnO proving that ZnO can be synthesized between multiple discrete sheets as well.
A.4 First excited states shapes

Figure A.7: Bulk wZnO First Excited state.

Figure A.8: gZnO First Excited State.

The first excited states of bulk wZnO and a 4-layer gZnO slab are shown in Figure A.7 and Figure A.8, respectively. These images show the shape of the states that are probed by the XANES simulations, and give an idea of how they have changed and how they may act differently with nearby atoms. The bulk ZnO and bulk-like atom of the gZnO show minor changes, mostly some shrinking of the central state and the emergence of small amounts of states near other Zn atoms. The biggest change is for the surface-like atoms which show a massive increase in the size of the first-excited states and an extension much farther out. This is where the pre-edge feature most likely originates.
Figure A.9: XAS Simulation of 4 layer gZnO sandwiched between graphene sheets.

Figure A.9 shows an optimized structure and relevant XAS spectra of different atoms in the 4-layer gZnO between graphene sheets. As can be seen, the strongest peak comes from a trigonal planar coordination. In fact, none of the tetrahedral coordinations, surface or otherwise, show a strong pre-edge feature, indicating that the planar coordination is critical in the sandwich structure for the strong pre-edge peak.

Figure A.10: XAS simulations of ZnO on SiO$_2$ covered by hydroxyls.
Figure A.10 shows XAS simulations of ZnO on SiO$_2$ covered by hydroxyls. As can be seen, only one spectra shows a pre-edge feature, but it is not sharp.

![Graph showing XAS simulations of ZnO and other compounds](image)

Figure A.11: XANES simulations of other Zn containing compounds.

Figure A.11 shows other compounds that may occur due to reactions or possible contaminants. None of the spectra match very closely to the experimental data. ZnSO$_4$ does have an energy match to the pre-edge feature, but has a very strong high energy peak that does not appear in any of the experimental spectra.
A.6 Full GIWAXS data for Fe$_2$O$_3$

![GIWAXS data graph](image)

Figure A.12: GIWAXS data of all Fe$_2$O$_3$ samples. Dotted line indicates the bulk Fe$_2$O$_3$ scattering.

Figure A.12 shows the GIWAXS scattering from all Fe$_2$O$_3$ sample types. The nanosheet scattering has a very weak peak near the bulk, indicating that the rGO is the main cause for the structural change. It has an unusual peak at 2.6 Å$^{-1}$ that is of unknown origin.
A.7 Doping concentration profiles

Figure A.13: Comparison of solution Al % versus measured Al% in solid samples.

Figure A.14: Comparison of solution Mg % versus measured Mg % in solid samples.
As mentioned previously, each element studied has drastically different intercalation rates. Each element was mixed with the Zn precursor as a standard. The intercalation efficiency is as follows: Al, Fe, Zn, and Mg. The wide variation seen in many of the samples may be due to several issues, including reused beakers containing small amounts of precursor even after cleaning and small amounts of precipitation.
A.8 Intercalated FIB images

Figure A.16: Side view image of a intercalated GO sample. a) Low mag version showing a dark line to the right of the interface layer. B) High Mag image showing the interface layer.

Figure A.16 shows the side view image of a sample intercalated with Zn precursor only. There was no high temperature treatment for crystallization, which also means there is no diffusion process. An interface layer is clearly visible, meaning that the complete interface layer exists because of the intercalation process and not diffusion through the GO or its defects. One other interesting feature is the dark line next to the interface layer. In other annealed samples, this layer appears. I considered it to be related to why the first few layers stick after annealing while the other layers separate and are removed by the expanding gas. However, it appears this layer also appears in intercalated samples. This may be indicating a separation of the top GO layer and the rest of the composite. This separation may aid the intercalation process and may be due to the weaker attachment of GO to SiO$_2$ than GO to itself. Another interesting result is that the ZnO in the composite appear to be randomly arranged instead of in thin sheets, indicating that heating plays a role in the morphology of the gZnO. However, this disorder has been observed in some FIB samples and may be a result of irregular stacking of the GO.
A.9 **Fe$_3$O$_4$ synthesis attempts**

![Figure A.17: Side view image and corresponding EDX scan of an Fe$_3$O$_4$ composite annealed in an Ar-96%/H$_2$-4% gas mixture for 1 hour at 600°C.](image)

It is clear from the EDX image that the iron oxide has coarsened into nanoparticles. The white dots everywhere on the HAADF are Pt, due to the high contrast in STEM. The damage is primarily a result of a catalytic reaction with Fe, as rGO can survive much higher temperatures in H$_2$ for reduction purposes. This may be a possible route with other elements that do not have a catalytic behavior.
A.10 Alumina nanosheet synthesis attempts

Figure A.18: AFM of an attempt at Alumina nanosheet synthesis. a) Optical image of the composite. B) AFM image of the area in the white dashed boxed area in a). It is clear there are only particles.

From Figure A.18, it is clear that alumina does not form clean nanosheets. Both thin and relatively thicker areas show only nanoparticle formation, indicating alumina is not compatible with the GO template method.
Appendix B Additional Methodology and Analysis

B.1 Characterization Details

AFM Measurements were performed in tapping mode using a Veeco D3100 atomic force microscope.

Side view lamella were fabricated at Argonne National Lab using FEI Nova 600 NanoLab Focused Ion Beam System at 30kV and 5kV or at the National Center of Electron Microscopy using FEI Strata 235 dual beam at 30kV and 5kV.

Plan view TEM Imaging, EDX, and nanobeam diffraction was performed at the Molecular Foundry at the National Center for Electron Microscopy using a FEI TitanX 60-300 microscope at 60 kV. The HRSTEM images were performed on a FEI Talos F200X TEM/STEM at 200kV or on a FEI TitanX 60-300 microscope. EELS measurements were taken using an monochromated F20 UT Tecnai.

Micro-PL measurements were performed using a custom-built setup using 266 nm excitation from a Coherent Chameleon femtosecond laser and tripler with a spot size of about 10 µm.

SEM Images were taken with a FEI Quanta 3D FEG with a secondary electron detector. XAS measurements have been performed at beamline 6.3.1 at the Advanced Light Source. Spectra are recorded at room temperature in total electron yield mode with a 30° grazing incidence angle between X-ray beam and sample surface. XMCD spectra were obtained under the same conditions under either 0.3 or 0.4T.

XPS measurements were obtained from a PHI 5600 XPS using a 2mm Al monochromatic source at 15 kV and 350 W with a neutralizer with a spot size of 400 µm.

GIWAXS measurements were performed at the Stanford Synchrotron Radiation Lightsource at beamline 11-2. Nanosheet and thin composites were taken at 0.05° incidence, while thick films and composites were performed at 0.1°. Radial integration plots from films were done using the entire plot, while composites and nanosheets integrated at low angles to prevent signal from the silicon substrate. The camera length was 150 mm and the scatter plots were taken for 180 seconds.

Raman measurements were performed on a Renishaw RM 2000 system with a Stellar Pro 514 nm laser.

Magnetic measurements were performed using a Quantum Design SQUID magnetometer (MPMS).

B.2 XAS and XMCD description

XAS is a deceptively simple measurement. It does not differ significantly from UV/VIS absorption spectroscopy, as it simply measures how much of a specific x-ray energy is absorbed. However, because core levels and large intensities are involved in the process, significant amount of detail can be observed in the spectra that can give a wealth of information. This technique measures the electronic structure in its base form, as the spectra depends heavily on available states above the core level. There are two major methods: EXAFS which uses single scattering contributions and XANES which involves multiple scattering (Figure B.1).
Both techniques look at changes in the absorption coefficient, $\mu$, which is given by:

$$\mu = \frac{\rho Z^4}{A E^3} \quad (B.1)$$

Where $\rho$ is the density, $Z$ is the atomic number, $A$ is the atomic mass, and $E$ is the X-ray energy.

At X-ray energies near the binding energy of a core electron there is an absorption edge due to the production of a photoelectron. This is the edge that is used to obtain information from X-ray Absorption Fine-edge Spectroscopy, specifically how $\mu$ changes near the edge. After absorption, the atom is in an excited state with an empty core level and a photoelectron and decays within a few femtoseconds, which is just long enough to observe some phenomenon for XANES. Decay usually occurs through fluorescence, in which higher shell electrons fall into core levels to release characteristic X-rays, that dominates at higher (>2keV) energies or Auger emission, in which the characteristic X-ray ejects a different electron, that dominates at lower energies (Figure B.2). Although XAS can be measured through transmission, due to the low thicknesses of my samples, total electron yield (TEY) is used instead.
Figure B.2: Schematic of the decay of the XAS process for TEY. The dotted line indicates the auger creation and the black line shows relaxation. This dynamic process modulates the absorption. Adapted from 165.

The TEY configuration does not measure the intensity of the X-ray beam after interactions with the sample, but instead utilizes photoelectrons. X-rays eject photoelectrons that leave behind holes. These holes are typically filled through auger decay that creates scattered secondary electrons. Multiple cascading scattering events occurs, and originate primarily from the first few nm of the material. AEY can potentially give even higher sensitivity to the surface, but typically requires additional setup and detectors. Electrons deep in the sample do not have enough energy to escape the material, which gives XAS significant surface sensitivity. The result is typically holes in the outer shells which are then filled utilizing a grounding electrical connection typically to the sample stage. The measured current then represents the intensity of the x-ray absorption.

The transitions that can occur rely heavily on the selection rules, while the fermi golden rule governs the intensity of the absorption. Fermi’s golden rule can be written as seen below, and is proportional to the square root of the absorption coefficient

\[ \mu(E) \propto |\langle i|H|f \rangle|^2 \]

Where \( <i| \) is the initial state, \( |f> \) is the final state and H is the interaction term. For this system, the initial state includes the incident x-ray, the relaxed core electron and no photoelectron. The final state is the combination of the core hole, photoelectron, and no x-ray. Core level electrons are localized on the absorbing atom, so the initial state is not affected by neighboring atoms. In contrast, photoelectrons are free to interact with neighboring atoms, so the final state relies heavily on neighboring atoms, and is the core reason for the sensitivity of EXAFS and XANES. A schematic for how EXAFS and XANES relate to each other on an energy scale appears in Figure B.3.
Figure B.3: Schematic comparison of EXAFS and XANES. EXAFS uses higher energy photoelectrons which have smaller wave differences than XANES. This makes a much more complicated analysis for XANES.

Turning specifically to XANES: XANES has a much larger signal and works well for very thin samples and lower concentrations. It is the preferred for samples with less than perfect sample conditions, as is the case for the zinc oxide samples. EXAFS, the preferred method for quantitative analysis, breaks down at low k-vectors of the waves and XANES takes its place. In regards to the cartoon in Figure B.3, the red curve can be seen as the ejected photoelectron wave, while the blue curve is the scattered wave traveling back towards the initial absorbing atom. EXAFS works well when the k-values of the two waves are similar and give a more regular interference pattern. XANES works at low k values when the two waves have significantly different k values and multiple scattering events become significant because of the lower energies. EXAFS on our samples was too difficult due to a greatly reduced signal. XANES is still sensitive to the same conditions as EXAFS: formal valence and coordination environment. XANES features occur in conditions in which the energy of the X-ray is very close to the absorption edge. At these energies, it is possible that the valence states are occupied. For example, a core level 1s transition to a 2p state may not occur if the 2p state is filled. This contributes to the information that can be obtained from XANES.

**XMCD description**

Dichroism refers to any kind of polarization dependent photon absorption. Anisotropies in charge or spin are often the source of this behavior. For X-Ray Magnetic Circular Dichroism (XMCD), the changes are from differently circularly polarized X-rays and their relation to the electron spin. Since the magnetic properties of most transition metals are determined by 3d valence electrons, L-edge absorption (2p to 3d) transitions are the main source of XMCD characterization and show a characteristic 2 peak spectra (L3 lower energy, L2 higher energy) due to spin-orbit
interactions of the 2p core shell. These two peaks can show multiplet structures in oxides, as the empty oxide states are more localized and can exhibit crystal field splitting and multiplet effects.

**Spin and Orbital Moments: X-Ray Magnetic Circular Dichroism**

(a) d-Orbital Occupation  
(b) Spin Moment  
(c) Orbital Moment

Figure B.4: Schematic of XMCD. A comparison of the a) XAS process and XMCD process for b) spin moment and c) orbital moments. In a) the spectrum is a typical XAS spectrum, while in b) and c) it is the XMCD spectra. The above schematics represent the difference in the XAS spectra under different polarized light. Figure adapted from 166.

**Circular Dichroism - Ferromagnets**

Figure B.5: Schematic of the XMCD process and the resulting changes in the XAS spectra. Fe metal is used as the example spectra. Different polarization, shown by the blue and red colors for different directions, create changes in the XAS spectra that correspond to the spin of electrons in certain states. Figure adapted from 166.

Transition metals can have up to 10 electrons in the d-band. For a typical magnetic material, the spin moment of the d shell comes from the difference in the spin-up and spin-down electrons/holes, so to measure the properties using XAS, the spin up/down electrons must be probed separately. This can be achieved by using right or left circularly polarized photons, which, as mentioned previously, can transfer angular momentum to the photoelectron.

A schematic of the XMCD process is shown in Figure B.4. The ejected photoelectron in XAS retains the transferred angular momentum as either spin, angular momentum, or a combination. If the photoelectron originates from a spin-orbit split level, e.g. the p_{3/2} level (L_{3} edge), the angular momentum of the photon can be transferred in part to the spin through the spin-orbit coupling. A magnetic material has a spin moment which is given by the difference in the
number of up versus down spin electrons (or holes in some cases). To measure this difference, right or left circularly polarized light is used to excite the photoelectron and transfer its angular momentum, such that the photoelectron carries the angular momentum as spin, angular momentum, or both. RCP light and LCP light transfer opposite momentum to electrons, creating opposite spin photoelectrons. Electric dipole transitions do not allow spin flip, so photoelectrons that have been given spin up can only be excited to spin up d hole states, and spin down photoelectrons only to spin down states. This means under circularly polarized light, the only electrons with one type of spin, due to the spin split valence shell, will be excited and can only transition to a state with the same spin, such that the intensity of the XAS is the number of empty d states of a given spin, demonstrated by example of Fe XAS spectra shown in Figure B.5. The difference in the spin states can be obtained by subtraction of the RCP and LCP XAS spectra, which can be used to determine the local geometry and oxidation state of the atoms from which these states originate.
B.3 XANES Simulation Details

The structure relaxations were performed using the VASP software package\textsuperscript{167,168} and the X-ray absorption spectra were computed using the PWscf code, distributed as part of the Quantum espresso source code package.\textsuperscript{169}

A bilayer of planar gZnO sheet (3×3 unit-cell) was initially sandwiched between two graphene sheets, and after structure optimization, the gZnO sheet is no longer perfectly planar, instead it becomes rippled such that almost half of the Zn atoms deviate from trigonal planar coordination as in the perfect planar gZnO to form tetrahedral coordination with 3 in-plane oxygen atoms and 1 out-of-plane oxygen, as shown in Figure 2.15c. Both of the structure relaxation and X-ray absorption simulations were performed using planewaves to represent the electronic wavefunction, and generalized gradient approximation to approximate the exchange-correlation functional.\textsuperscript{170} PAW type potentials were used in the structure relaxation in VASP\textsuperscript{171,172} and ultrasoft pseudopotentials are used in the PWscf X-ray absorption calculations.\textsuperscript{173} To simulate the Zn L-edge spectra, a modified Zn pseudopotential was used with a removed core-electron from the Zn 2p state. Large discrepancies of Zn L-edge spectra are observed for gZnO/graphene composite, where the pre-edge feature is red shifted in the simulated spectrum compared to experiment. This is likely due to the semi-local generalized gradient approximation used in the simulation that fails to correctly predict the relative positions of Zn 4s and 4d state at the bottom of conduction bands. A number of simple Hubbard U models have been applied to correct the band alignment in ZnO, and if we pick a set of U parameters (U_{Zn,4d} =12.8 and U_{O,2p} = 5.29) as recommended by Ref.\textsuperscript{174}, the pre-edge feature indicated by the red arrow in Figure 2.15 will be blue shifted by ~ 0.5 eV. Similar U model has even been proposed for Zn 4s state.\textsuperscript{175} Ideally, more sophisticated hybrid functional or advanced excited state theory should be used to better predict the position of Zn 4s and 4d under photon excitation, which is currently under investigation and is beyond the scope of this dissertation.
Bibliography


41. Freeman, C. L., Claeyssens, F., Allan, N. L. & Harding, J. H. Graphitic nanofilms as
48. Dulub, O., Boatner, L. A. & Diebold, U. STM study of the geometric and electronic structure of ZnO (0 0 0 1)-Zn,(0 0 0 Γ)-O,(1 0 Γ 0), and (1 1 2 Γ 0) surfaces. Surf. Sci. 519, 201–217 (2002).
49. Dulub, O., Diebold, U. & Kresse, G. Novel stabilization mechanism on polar surfaces: ZnO (0001)-Zn.


Nemes-Incze, P., Osváth, Z., Kamarás, K. & Biró, L. P. Anomalies in thickness
130. Tilley, S. D., Cornuz, M., Sivula, K. & Grätzel, M. Light-Induced Water Splitting with Hematite: Improved Nanostructure and Iridium Oxide Catalysis. Angew. Chemie 122,
118


