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Novel Two-dimensional Nanomaterials and Their Gas Sensing Properties

Haihui Pu
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NOVEL TWO-DIMENSIONAL NANOMATERIALS AND
THEIR GAS SENSING PROPERTIES

by

Haihui Pu

A Dissertation Submitted in Partial Fulfillment of the
Requirements for the Degree of
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ABSTRACT

NOVEL TWO-DIMENSIONAL NANOMATERIALS AND THEIR GAS SENSING PROPERTIES

by

Haihui Pu

The University of Wisconsin-Milwaukee, 2015

Under the Supervision of Professor Junhong Chen

Graphene, an atomic thin two-dimensional (2D) material with C atoms arranged in a honeycomb lattice, has sparked an unprecedented research interest across various scientific communities since its initial mechanical isolation in 2004. The linear energy dispersion with respect to the momentum within 1 eV around the Fermi level at the high symmetric K (Dirac) points in the Brillouin zone renders graphene a wonder material for scientists. However, graphene’s semimetallic nature significantly limits its high-end applications, e.g., in digital logic circuits. Therefore, continued efforts in opening the band gap for graphene and in searching for novel 2D semiconducting materials are rewarding.

Various methods have been proposed for generating band gaps in graphene and other related 2D nanomaterials; however, few can be utilized to tune the band gap over a wide range on the same device and many are realized at the cost of severe degradation of
carrier mobility. Recently, a new graphene-based crystalline structure, graphene monoxide (GMO), has been discovered based on electron diffraction observations during \textit{in situ} thermal reduction of multilayer graphene oxide (GO) under vacuum in a transmission electron microscope (TEM) chamber. Supported by infrared spectroscopy and first-principles calculations, the new 2D material was identified as a two-phase hybrid containing GMO domains that evolve in the graphene matrix. GMO extends the electronic property of a graphene derivative into the semiconductor world, enabling potential applications for nanoelectronics. Another route to address the graphene band gap bottleneck is to search for new 2D nanomaterial candidates, among which 2D transition metal dichalcogenides (e.g., MoS$_2$) and black phosphorus (BP) are attracting significant attention. Although both are layered structures and have a tunable band gap, a higher carrier mobility and a wider band gap ranging from 0.3 eV for bulk-like BP to 1.8 eV of monolayer BP make BP an outstanding candidate for future electronic applications. Conductance-based nanoscale gas sensors based on these 2D nanomaterials are attractive due to their superior sensitivity/selectivity and relatively low cost. Experimental studies have shown that in general semiconducting materials exhibit better sensitivity than insulating/metalllic materials. Thus, it is crucial to understand the gas sensing mechanism of semiconducting materials and to gain better insights into the performance enhancement.

This thesis aims to explore the fundamental properties of novel 2D nanomaterials and to understand their gas sensing performance. Various GMO properties were calculated using density functional theory (DFT)-based techniques. Infrared (IR) spectra of GMO were calculated for both pure GMO and GMO domains embedded into the graphene
matrix to facilitate its identification during formation. GMO has three IR active modes that are distinctive from those of graphene and GO. The electronic and mechanical properties of GMO were predicted to illuminate its potential applications in semiconductor devices. The band gap of GMO can be tuned over a wide range from 0 to 1.35 eV. The capability of heat removal in intrinsic GMO was also simulated with and without planar lattice strains and compared with that of graphene and silicon. GMO exhibits a superior thermal conductivity (>3,000 Wm$^{-1}$K$^{-1}$), 80% of that of graphene along the armchair direction for large lateral sample sizes (>5 µm). The magnetic properties of zigzag graphene nanoribbons (ZGNRs) induced by GMO domains (or epoxy pair chains) were investigated. The epoxy pair chains can generate finite spin moments in ZGNRs irrespective of the spin coupling between ribbon edges.

The gas sensing properties of selected 2D nanomaterials were characterized both theoretically and experimentally. First, we developed statistical thermodynamics models with the gas binding energy from DFT calculations as the only input to characterize the monolayer gas adsorption density on graphene and BP thin films. Our statistical thermodynamics models can successfully predict the gas adsorption density with high accuracy compared with experimental data. Second, an analytical model was established to interpret why semiconducting materials are preferred for gas sensing applications using a BP thin film-based gas sensors as an example. The sensitivity model suggests that the optimum thickness of BP thin film is from several to 10+ nm, corresponding with a band gap of 0.3 to 0.6 eV. Third, van der Pauw and Hall measurements were performed to obtain the sheet resistance, the carrier concentration, and the carrier mobility for thermally-reduced GO (TRGO) at various temperatures to illuminate relative
contributions from the carrier concentration and the carrier mobility to the sheet resistance change upon gas adsorption, which suggests that the conductance change upon gas adsorption mainly results from the carrier concentration change. Finally, the sensitivity enhancement from the nanocrystalline particles deposited on the surface of graphene-base materials was also investigated.
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In August 2010, I was lucky enough to join Prof. Junhong Chen’s research group and began my doctoral program at the University of Wisconsin-Milwaukee (UWM). The last five years didn’t fly without difficulties, but it was rewarding and I obtained both personal and professional growth. I am deeply indebted to my family for their both financial and spiritual support during my Ph.D. program. I also express my sincere appreciation to my supervisors, Prof. Junhong Chen and Prof. Michael Weinert, for their insightful guidance in carrying out my dissertation research, and I am grateful to, Prof. Marija Gajdardziska-Josifovska and Prof. Carol Hirschmugl from the UWM Physics Department and Dr. Sonny Rhim from Northwestern University for their comments and suggestions during the research, as well. I also thank many former and current group members, including Dr. Ganhua Lu, Dr. Pengxiang Wang, Dr. Shun Mao, Dr. Kehan Yu, Dr. Shumao Cui, Dr. Zhenhai Wen, Dr. Suqin Ci, Dr. Yang Zhang, Dr. Jingbo Chang, Dr. Xingkang Huang, Dr. Yang Hou, Dr. Taizhong Huang, Dr. Yu Xie, Dr. Jianbin Zang, Guihua Zhou, Xiaoru Guo, Ren Ren, Xiaoyu Sui and Dr. Yantao Chen for their various academic and daily-life help. And I greatly cherish the time spent with them. Finally, I would like to acknowledge the financial support from the National Science Foundation (CMMI-0856753 and CMMI-0900509), from the Research Growth Initiative Program of UWM, and from the UWM Distinguished Dissertation Fellowship. The theoretical work was carried out at the UWM high performance computing center and I thank Dr. Jason Bacon for his technical support.
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CHAPTER 1 NOVEL 2D NANOMATERIALS AND NANOGLAS GAS SENSORS

1.1 Carbon-based Nanomaterials

1.1.1 Graphene

Graphene is a 2D atomic layer with C atoms arranged in a honeycomb lattice. It is the fundamental building block of the carbon allotrope structures, such as zero-dimensional (0D) fullerenes, one-dimensional (1D) nanotubes, and three-dimensional (3D) graphite. Given its importance, it is quite surprising that graphene is the last one being studied extensively among all known carbon allotropes, which is mainly due to the instability problem of 2D crystals. It has long been shown theoretically that thermal fluctuation due to the flexural mode at a finite temperature would destroy the long range order in 2D crystals\(^1\)\(^2\). However, it came as a huge surprise when Professors Andre Geim and Kostantin Novoselov’s group from Manchester University in the UK in 2004\(^3\) experimentally isolated a single layer of graphene via mechanical exfoliation of graphite flakes using scotch tape, which eventually led to their 2010 Nobel Prize in Physics. Independently, Professor Walt de Heer from Georgia Institute of Technology successfully produced epitaxial graphene from silicon carbide precursors and measured the electronic properties of monolayer graphene in 2004\(^4\). Subsequently, Professor Philip Kim’s group from Columbia University experimentally observed the quantum hall effect and Berry’s phase in graphene in 2005\(^5\). These pioneering studies and many others not
mentioned here contribute to the unveiling of the various exotic properties of graphene and since have sparked unprecedented intense research interest on graphene.

Fig. 1.1 (a) shows the hexagonal lattice of graphene with two types of edges labeled. The primitive cell of graphene is a rhombus with a basis of two nonequivalent C atoms A and B situated at the two sublattices. In real space, the cell can be described by the two basic vectors $a_1$ and $a_2$ intersecting at angle of 120° and with equal length of 2.46 Å. In the reciprocal space, shown in the inset of Fig. 1.1 (b), the first Brillouin zone (BZ) boundaries enclose a hexagon with six corners alternatively labeled by K and K'. The reciprocal basis vectors are now described by $b_1$ and $b_2$ with an angle of 60° between them. It can be seen that K and K' can be related to each other by the time reversal
symmetry operation. Fig. 1.1(b) shows the band structure of graphene along the high
symmetry lines in the first irreducible BZ (IBZ). A peculiar feature of the graphene band
structure is that the conduction band and the valence band touch each other
symmetrically at the charge neutrality point K (K′) with the linear energy momentum
dispersion around the Fermi level. Therefore, graphene is usually considered as
semimetal or zero-gap semiconductor.

The band structure of graphene clearly suggests that its electronic properties are mainly
determined by the states around the Fermi level (namely, at the charge neutrality point).
This could also be reflected from the point view of orbital hybridization. The single C
atom has four valence electrons occupying the 2s², 2px¹ and 2py¹ orbitals. Upon the sp²
hybridization, one of the electrons in the 2s orbital is promoted into the 2pz orbital, and
the 3-fold symmetric hybridized orbitals are generated by the superposition of the 2s, 2px
and 2py orbitals, leaving the 2pz orbital intact. In the honeycomb lattice, each C atom
forms three σ bonds with the neighboring C atoms via the planar sp² hybridized orbitals,
while the overlap of the remaining free 2pz orbitals present π symmetry orientation. The
planar σ bonds have a much higher bond strength than π bonds perpendicular to the
carbon plane. Thus, π (bonding) and π*(antibonding) bands are located closer to the
Fermi level than σ (bonding) and σ *(antibonding) bands. In other words, the π and σ
bonds are primarily responsible for the electronic and mechanical properties of graphene,
respectively. And the Dirac equation is adopted to depict the linear dispersion in terms of
massless relativistic particles. Therefore, the π electrons in graphene are called Dirac
fermions and the charge neutrality point is referred to as Dirac point. Based on the Dirac
equation, one could determine that the Dirac fermions in graphene possess an effective
Fermi velocity of around 300 times smaller than the speed of light. This makes graphene a reliable system for physicist now to study the quantum electrodynamics phenomena in the lab. Over the years, many exotic properties of graphene have been experimentally unveiled, such as the fractional quantum hall effect, Andreev reflection and Klein tunneling, and superior electron mobility (200,000 cm$^2$/Vs at room temperature).

Owing to the success of continuous production using chemical vapor deposition (CVD), graphene, as a host material, is now increasingly being used in nanoscience and nanotechnology. For example, graphene has now found uses in a variety of applications, to name a few, as heat dissipation pads, transparent electrodes in solar cells, flexible displays in optoelectronic devices, and as field emission sources.

Although graphene has been envisioned as a replacement for Si in digital logic circuits due to its exceptional electron transport properties, the gapless nature of the massless Dirac fermions, however, severely limits the pace of graphene in the semiconductor world, in which Si is still dominant in digital logic circuits. Despite that pure graphene-based transistors with a cutoff frequency as high as 300 GHz have been achieved, the poor on/off ratio of ~1,000 at room temperature is still far away from that (>10,000) of silicon transistors.

Significant effort has been devoted to identifying mechanisms to tailor the energy band gap of graphene, including application of a gate voltage, interactions with substrates, and the formation of nanostructures such as nanoribbons, graphene nanomeshes, and graphene quantum dots. Opening of a band gap of 0.25 eV has been reported for bilayer graphene through the gating effect, and monolayer graphene grown epitaxially on SiC.
substrates produces a similar bandgap (~0.26 eV) \(^{20,21}\). Armchair graphene nanoribbons (AGNR) achieve band gaps around 1 eV for widths below ~1.5 nm\(^{25,26}\), but with considerable degradation of electron mobility\(^{27}\). Moreover, variations in the band gap are inevitable due to inherent edge disorders\(^{26}\), which is also true for graphene nanomeshes and quantum dots. Since precision control of the edge type and its purity is a prerequisite for GNR- or its derivatives-based nanoelectronics, to usher in the next generation of electronic devices based on graphene, it still demands new approaches to efficiently engineer the band gap.

Due to the strong \(\sigma\) bond, graphene could also play a role in heat dissipation in future nanoelectronics. Semiconductor electronic devices have been steadily decreasing in size and are now in the nanometer regime. Further reductions in the scale of the devices, however, is limited by the ability to dissipate heat from the device, because of the significantly enhanced heat generation rate per unit surface area and the decreasing thermal conductivity of device components\(^{28}\). For instance, the heat generation rate for nanoscale devices can reach as high as that of a rocket nozzle (1,000 Wcm\(^{-2}\)) and the thermal conductivity reduces significantly from 150 Wm\(^{-1}\)K\(^{-1}\) for bulk Si to 10 Wm\(^{-1}\)K\(^{-1}\) for Si nanowires\(^{29}\). Therefore, heat removal is a major bottleneck to the further miniaturization of logic circuit chips.

Graphene has been shown to exhibit superior room temperature thermal conductivity, which varies from 3,000 to 5,000 Wm\(^{-1}\)K\(^{-1}\) (for a suspended monolayer graphene),\(^{30,31}\) but degrades to 600 Wm\(^{-1}\)K\(^{-1}\) when placed on a SiO\(_2\)/Si substrate.\(^{11}\) Pure graphene has been used for heat dissipation on its own or as part of nanocomposites with metals.\(^{32}\) As
opposed to graphene, semiconducting GNRs have been extensively demonstrated in transistor applications\textsuperscript{33}. GNRs with lateral sizes between 2 and 11 nm have thermal conductivities ranging from 1,000 to 7,000 Wm\textsuperscript{-1}K\textsuperscript{-1} for both armchair and zigzag edges. However, a bandgap occurs only in AGNRs at finite temperature, and both the bandgap\textsuperscript{34,35} and the thermal conductivities\textsuperscript{36,37} have a strong dependence on the ribbon width.

Apart from potential applications in nanoelectronics, it is also worth exploring the spin freedom of graphene and its use in spintronics. Intrinsic graphene is nonmagnetic and magnetism can be induced by vacancies\textsuperscript{38} and magnetic impurities\textsuperscript{39}. In addition, the zigzag GNR (ZGNR) is theoretically predicted to be in a magnetic ground state, with a small band gap around Fermi level at 0 K where the edge states are spin-polarized\textsuperscript{40}. The edge atoms are ferromagnetically ordered along one edge and antiferromagnetically ordered between the two edges. Upon the application of a transverse electric field, the spin degeneracy is lifted with the bandgap increased for one spin and decreased for the other. Therefore, the ZGNR becomes half metal when the electric field is large enough (> 0.1V/Å)\textsuperscript{40}. In fact, this electric potential could also be effectively achieved by decorating the edges of ZGNR with different functional groups\textsuperscript{41}. The half-metallic feature can be utilized to design graphene-based spin valves or spin field-effect transistors \textsuperscript{42}.

In summary, graphene is a 2D atomic thin film with C atoms arranged in the honeycomb lattice. While graphene possesses superior electronic and thermal properties, the zero bandgap of pristine graphene limits its potential applications in digital circuits. As a result, great opportunities exist to create a band gap in graphene using various approaches,
including interaction with substrate, cutting into nanoribbons or nanomeshes. In addition, the ground state of ZGNR is spin polarized with the spin aligned ferromagnetically along the edge and antiferromagnetically across the two edges, but the total magnetic moment is zero. Interestingly, ZGNR will become half metallic upon an external electric field, which closes the bandgap for one spin and widens that for the other. Despite the above efforts, it is still worth exploring new avenues to engineer the bandgap of graphene and its magnetic properties for future electronics and spintronics applications.

1.1.2 Graphene Oxide

Fig. 1.2 Schematic structure of monolayer GO with functional groups (1) epoxide, (2) phenol, (3) hydroxyl, (4) carbonyl, (5) carboxyl, (6) lactone, and (7) quinone.43

Graphene oxide (GO), namely, the oxidized graphene, can be synthesized in large quantities by oxidizing inexpensive graphite powders using strong oxidants. During the oxidation process, graphite powders are exfoliated and broken into layers with increased interlayer distance; the landscape of the $sp^2$ carbon network is modified with oxygen-
containing functional groups, defects, and holes. Despite its first experimental synthesis more than one and half centuries ago, the atomic structure of GO is still elusive today due to its nonstoichiometry. By using the $^{13}$C and $^1$H nuclear magnetic resonance (NMR) spectra, Lerf et al.\textsuperscript{44} revisited the structure of GO in 1998 and assigned critically the chemical shift line around 60 ppm to 1, 2-ethers instead of 1, 3-ethers; they also confirmed the assignment of the line around 70 ppm to hydroxyls. Now the three major chemical shift peaks around 60, 70, and 130 ppm have been commonly accepted and assigned to epoxy, hydroxyl and sp$^2$ carbon, respectively\textsuperscript{44-52}. Previously, epoxy and hydroxyl were determined to be two major functional groups across the basal plane in GO. In 2009, Gao and Ajayan et al.\textsuperscript{53} further assigned the peak around 101 ppm to five- or six-membered-ring lactol decorated on the edge of holes in GO flakes.

Fig. 1.2 illustrates the possible oxygen-containing functional groups (epoxy:-C-O-C-,
hydroxyl:-C-OH, carbonyl:-C=O, carboxyl:-O-C=O, phenol: -CH$_2$-OH, lactone: -C-O-C=O, and quinone: -C=O-C=O). Their arrangements across the carbon network are critical for obtaining a thorough view of the GO structure. Although the consensus is that GO is decorated by epoxies and hydroxyls, which are randomly distributed across the carbon backbone, and that carbonyls, phenols, lactone, quinones, and carboxyls are minorities and mainly attached on the edges, some uncertainty still revolves around the morphology of GO, e.g., whether it has tiny islands of structural ordering. To gain information about the distribution of major functional groups, two- and multi-dimensional NMR spectra conducted by Ruoff’s group revealed that epoxy and hydroxyl were close to each other, with some tiny islands of pure epoxies or hydroxyls\textsuperscript{46,47}. The major peaks in the NMR discribed above were related to the carbon atoms single-bonded
to oxygen atoms. X-ray photoelectron spectroscopy (XPS), however, showed evidence that $sp^2$ carbon atoms are accompanied by three other carbons connected with epoxy or hydroxyl (single-bonded), carbonyl (double-bonded), and carboxyl (triple-bonded) groups, respectively. Near-edge X-ray absorption fine structure for O-K edge suggested that the carbonyls in GO are arranged on the carbon layer on average, and there is locally ordered structure from some oxygenated functional groups. Again, this ordered structure was elusive until a scanning tunnelling microscopy (STM) study on oxidized exfoliated graphene sheets showed an ordered structure exists from pure epoxies arranged in a rectangular lattice on both sides of the carbon layer. However, once hydroxyls are present, the oxidized regions in GO become amorphous and the ordered structure can only be developed under specific conditions.

Considering that the carbon lattice in GO is conserved during the oxidation process and that the transport properties of graphene are totally ruined by the functional groups, the purpose of thermal reduction is to remove the oxygen groups and maximally restore the transport properties of graphene. GO can be reduced either chemically or thermally with tailored properties by controlling the reduction conditions. As such, the morphology of TRGO is different from that of pure graphene in several respects. With the carbon loss and some oxygen atoms remaining after thermal reduction, the line defects, holes, and lattice mismatch-induced crumples are prominent in the carbon skeleton of TRGO. Although "defective" graphene loses some electrical conductivity/mobilities, the defects also offer extra functions to graphene to enable many interesting applications that are impossible for pure graphene. For example, "defects" make it possible to make surfactant-free graphene colloids and are advantageous in specific applications like gas
sensors. The conductivity of RGO could reach as high as $5.7 \times 10^4 \text{ S} \cdot \text{m}^{-1}$, which is several orders of magnitude larger than that of GO ($10^{-8}$ - $10^{-5} \text{ S} \cdot \text{m}^{-1}$), on the same order of magnitude as that of graphite ($8.4 \times 10^4 \text{ S} \cdot \text{m}^{-1}$) and about two orders of magnitude lower than that of graphene ($5$ - $6.4 \times 10^6 \text{ S} \cdot \text{m}^{-1}$). Hence, preparation of graphene through the reduction of GO is most promising for the mass-production of graphene-based materials among the various approaches employed to synthesize graphene, such as the micromechanical exfoliation of graphite, CVD, epitaxial growth and chemical intercalation.

In summary, GO is nonstoichiometric with main functional groups of epoxide and hydroxyl arranged across the carbon plane and minority groups such as carbonyl and carboxyl attached to its edges. GO is insulating, in stark contrast to metallic graphene, greatly hindering its future applications in electronic devices. However, most functional groups in GO can be removed by chemical or thermal reduction methods. RGO, on the other hand, offers tunable properties and thus enables various applications through controlled reduction to induce defects and to tailor remnant functional groups.

1.1.3 Graphene Monoxide

The oxygenated functional groups in GO can be removed thermally through the concurrent and even synergistical release of gas molecules of H$_2$O, CO$_2$ and CO. During the reduction process, the picture for the evolution of water molecules is clear, in which hydrogen atoms dissociate from hydroxyls and combine with other nearby hydroxyls to form water molecules, leaving the atop oxygen atoms to form epoxies. Nevertheless,
the mechanism of CO₂ and CO formation is still elusive at this time. Generally, the chemical composition of GO varies from C_{1}O_{0.17}H_{0.08} to C_{1}O_{0.49}H_{0.2} depending on the synthesis method and oxidation time^{49,80}. Despite the amorphous feature of GO and TRGO, it is possible for the epoxides to arrange in a crystalline manner on graphene. There are two scenarios reported so far. First, theoretical calculations predicted that the arrangement of epoxides is energetically favorable when they are bonded to both sides of graphene, forming a small island with O:C of 1:2 (C₂O)^{50,81}, which can be described in a rectangular unit cell observed experimentally by NMR^{46} and STM^{58}. Second, graphene can be further oxidized with a O:C ratio up to 1:1(C_{1}O_{1}) if the sp² carbon bond in its primitive cell is bridged two epoxide groups above and below the carbon plane^{82}. This structural configuration, called graphene monoxide (GMO), recently has been shown theoretically to be more energetically stable^{82} than the C₂O structure, and observed experimentally through thermal reduction of multilayer GO inside a transmission electron microscopy (TEM) chamber^{83}. GMO is a new crystalline 2D nanocarbon material, which is predicted to be a semiconductor^{82,83}.

1.2 Black Phosphorus

BP, the most stable allotrope in the phosphorus family, is a layered 2D structure with the interlayer spacing of 5.3 Å as shown in Fig. 1.3. The monolayer of BP is called phosphorene, and each phosphorus atom forms three bonds with its nearest neighbors in the puckered form, showing two distinctive crystalline directions: armchair vs. zigzag. In contrast to graphene that is a semimetal, or MoS₂ that is a direct energy gap semiconductor at monolayer (1.9 eV) and becomes indirect from bilayer (1.6 eV) up to
the bulk limit (1.3 eV)\textsuperscript{64,65}, BP is semiconducting with the direct energy gap ranging from ~2.0 eV for monolayer phosphorene to ~0.3 eV for bulk BP. (The thickness-dependent band gap of a black phosphorus film is partly due to the interlayer van der Waals interaction\textsuperscript{86}, as suggested by the observation that the electronic conductivity of BP reduces after lithium intercalation\textsuperscript{87}.)

Fig. 1.3 (a) Perspective view of black phosphorus, (b) Top view of monolayer phosphorene with armchair and zigzag directions indicated.

Despite its semiconducting nature, the room temperature electron mobility (0.5-3 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1})\textsuperscript{88} in single layer MoS\textsubscript{2} is too low for practical application in electronic devices; it was later rediscovered to be ~ 200 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} from dual-gate measurements\textsuperscript{89} with debate\textsuperscript{90}. However, the hole mobilities extracted from the Hall measurements are 1,000 and 600 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} along the armchair and zigzag directions for a 15-nm BP film at 120 K, respectively\textsuperscript{91}. At room temperature, the field-effect mobility is the highest, up to ~1,000 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} for a film thickness of ~10 nm\textsuperscript{92}, and then degrades to 205 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} on
5 nm BP\textsuperscript{91}. In addition, the well-behaved p-type BP transistors show good current saturation with a large on-off ratio (exceeding $10^5$)\textsuperscript{91,92}. Thus, mono- to few-layer phosphorene are promising for electronic applications due to their finite direct band gaps and high carrier mobilities. Moreover, BP thin film-based devices can be considered as promising candidates for future electronics operated in the multi-GHz frequency range and beyond. For instance, the measured short-circuit current-gain cutoff frequency $f_T$ in 300 nm channel length devices is 12 GHz with a maximum oscillation frequency $f_{\text{max}}$ of 20 GHz\textsuperscript{93}.

Due to its unique puckered crystal structure, phosphorene has superior flexibility and the mechanical strain would significantly modify its electronic property. The band gap will be enlarged for tensile strain up to around 4\% and then begin descending\textsuperscript{94}. It has also been shown that 4-6\% biaxial or uniaxial strain will switch the preferred conducting direction between the armchair and zigzag directions\textsuperscript{95}. Furthermore, a semiconductor-metal transition can be induced by the out-of-plane deformation\textsuperscript{96} and the compressive strain\textsuperscript{97}. Phosphorene can sustain tensile strains up to 27\% and 30\% in the zigzag and armchair directions, respectively\textsuperscript{98}, primarily because a tensile strain stretches the pucker of phosphorene without significantly elongating the P-P bond lengths, resulting in its in-plane Young's modulus (41.3 GPa in the armchair direction and 106.4 GPa in the zigzag direction\textsuperscript{99}) one order of magnitude smaller than that of graphene. In addition, a negative Poisson's ratio is predicted in the out-of-plane direction under uniaxial deformation along with the pucker direction\textsuperscript{100}. 
The hinge-like structure of phospherene makes it strongly anisotropic with distinctive properties along different crystalline directions. Optically, BP shows strong absorbance for the incident light polarization along the armchair direction, in contrast to near transparency for the incident light polarization along the zigzag direction, making it a future candidate for linear polarizers applications\textsuperscript{101}. Thus, the angle-resolved polarized Raman spectroscopy can be used to identify the crystal orientation of BP sheets (the zigzag and armchair directions) since the Raman intensities of $A_{1g}$, $B_{2g}$, and $A_{2g}$ modes of BP depend on both the polarization angle and the sample rotation angle. It was found that the $A_{2g}$ mode intensity reaches the relative larger (or smaller) local maximum values when the polarization direction of scattered light is parallel to the armchair (or zigzag) direction\textsuperscript{102}. Multilayer BP has a photoresponsivity two orders of magnitude larger than graphene\textsuperscript{103}. The optical absorption spectra of multilayer BP can be tuned sensitively with respect to the film thickness, strain and light polarization\textsuperscript{104}. For example, the exciton binding energy is found to be 0.40 eV for compressive biaxial strain of -8\%, and it becomes 0.83 eV for a tensile strain of 4\%\textsuperscript{105}. The collective electronic excitations in the system also exhibit a strong anisotropy\textsuperscript{106}.

The distinct anisotropy in optical, electronic, and mechanical properties make BP promising for thin-film electronics, infrared optoelectronics, and novel device applications, such as thermal energy scavenging\textsuperscript{107} since BP is a potential medium-high temperature thermoelectric material\textsuperscript{108}, negative electrodes with both high capacity and high-rate performance in all-solid-state lithium rechargeable batteries with sulfide electrolytes\textsuperscript{109}, an optoelectronic material for hyperspectral imaging applications with high-contrast ($V > 0.9$) images both in the visible (532 nm) as well as in the infrared
(1,550 nm) spectral regime\textsuperscript{110}, hydrogen storage material with a capacity as high as 8.11 wt.$\%$\textsuperscript{111}, anode for both Na-ion and Li-ion batteries\textsuperscript{112}, nanoelectromechanical resonator vibrating at high and very high frequencies (up to similar to 100 MHz)$^{113}$, solar energy harvesting (based on a p-type BP/n-type monolayer MoS\textsubscript{2} van der Waals p-n heterojunction\textsuperscript{114}), and fast photon detection with excitation wavelengths from the visible region up to 940 nm and a rise time of about 1 ms\textsuperscript{115}.

Since BP is a 2D semiconductor with a tunable bandgap with respect to layer number/film thickness, BP is ideal for gas sensor applications. First-principles studies\textsuperscript{116} have shown that monolayer phosphorene exhibits superior sensing performance even better than graphene and MoS\textsubscript{2}. The adsorption strength between gas molecules are strong for NO, NO\textsubscript{2} and NH\textsubscript{3}, up to 0.86eV, 0.62eV and 0.50eV, respectively\textsuperscript{116}. The predicted current-voltage from the nonequilibrium Greens function method further shows the superior sensitivity and selectivity despite the large anisotropy of one to two orders of magnitude of conductance along the armchair/zigzag directions\textsuperscript{116}. However, the superior sensitivity is only characterized in terms of the adsorption strength or the charge transfer amount. Other aspects in gas adsorption density and the bandgap/film thickness dependent sensitivity are still missing and deserve further study.

Despite the various potential applications, it is a prerequisite to produce large scale BP with good quality and stability for its various applications. A low-pressure transport reaction route has been demonstrated for realizing the effective and scalable synthesis of BP with high crystallinity\textsuperscript{117}. Few-layer phosphorene nanosheets can then be produced by the liquid or mechanical exfoliation of BP\textsuperscript{118}. For the exfoliated thin BP crystals, however,
significant surface roughening can occur within 1 h upon exposure to ambient conditions\textsuperscript{119}. This effect is more prominent for thinner films. It as found that O\textsubscript{2} saturated H\textsubscript{2}O reacts irreversibly with BP to form oxidized phosphorus species, leading to the large increases in threshold voltage, on/off ratio and mobility degradation\textsuperscript{120}. Thus, practical applications of few-layer phosphorene necessitate the surface passivation.

1.3 Nanoscale Gas Sensors

1.3.1 Gas Sensor Working Principles
Gas sensing has become increasingly important in various applications such as industrial pollutant gas leakage detection (e.g., NO\textsubscript{2}, NH\textsubscript{3}, H\textsubscript{2}S, SO\textsubscript{2}, CO), environmental monitoring, and homeland security. Much effort has been devoted to developing novel platforms for gas sensing with high sensitivity, selectivity, stability, and fast response and recovery. In principle, a gas sensor works by transforming the gas adsorption into detectable signals and many types of gas sensors have been designed. Thermometric gas sensing, for example, also known as calorimetric gas sensing, is used to indirectly detect combustible gases by measuring temperature changes during the burning process of a specific flammable gas in certain concentrations of oxygen\textsuperscript{121}. Magnetic gas sensors consist of magnetic materials with porous cores and an induction coil wrapped around them, and the inductance of the coil varies with the gas adsorption-induced change in the magnetic properties of these cores\textsuperscript{122}. Surface acoustic wave gas sensing takes advantage of the piezoelectric effect of the acoustic sensor, whose frequency can be shifted by the adsorption of target gas species, temperature, or conductivity changes by chemical reactions, and surface stress variations due to the substitution of atoms or molecules\textsuperscript{123};
Optical gas sensors detect gas species by monitoring its characteristic optical adsorption\textsuperscript{124}; and resistance or conductance gas sensors measure the change in the system resistance or conductance due to the gas adsorption\textsuperscript{125}.

The conductance-based gas sensors have attracted significant attention due to their relatively low cost and high performance. Many platforms have been designed and used to detect specific gases. For instance, graphene\textsuperscript{126} and RGO\textsuperscript{62} are 2D nanomaterials with a large surface-to-volume ratio indicative of rich adsorption sites. Pure graphene has been shown to be sensitive to NO\textsubscript{2} and NH\textsubscript{3}, and the sensitivity can reach the level of a single NO\textsubscript{2} molecule\textsuperscript{126}. However, graphene is barely sensitive to CO\textsuperscript{127}. RGO can expand the sensitivity of gas species due to the remnant oxygen containing groups and defects after reduction\textsuperscript{61}. Improvement in the gas sensing performance such as sensitivity and selectivity largely comes from the innovation in conducting (sensing) materials.

The hybrid nanostructure composed of carbon allotropes and nanoparticles works as a gas sensor and each nanocomponent functions differently. The selectivity can be enhanced by depositing crystalline nanoparticles such as SnO\textsubscript{2}\textsuperscript{128}, WO\textsubscript{3}\textsuperscript{129}, Ag\textsuperscript{130}, and Pt\textsuperscript{131} on graphene, RGO, or carbon nanotubes (CNTs). Depending on the surface coverage by nanoparticles, the underlying carbon is either partially exposed to target gases or fully covered with nanoparticles. Thus, the carbon skeleton mostly acts as the conducting channel. The coated nanoparticles, however, can directly interact with the gases, which leads to a change in the conductivity of the sensing system. For chemically noninteracting gas species, gas molecules normally adsorb and desorb simultaneously on the nanoparticle surface. The adsorption and desorption rate can differ depending on the
gas concentration and the working temperature-related adsorption strength. The equilibrium can be realized after a certain duration of time, which can be experimentally observed as a plateau of the system resistance after gas exposure. Generally, this type of gas sensor is reversible and reusable since the gas adsorption is physical, i.e., physisorption. Some gases, on the other hand, can chemically interact with the nanoparticles. For instance, the precious metal Ag can be oxidized in air by dissociating oxygen molecules spontaneously, and thus gas sensors will be normally smeared by these chemically reacting gas species. However, this effect can also be used to design new types of gas sensors, especially for H$_2$ molecules which are hard to detect in most gas sensing systems due to their small atomic mass and weak reactivity. H$_2$ detection can be realized by carbon allotropes coated with Pt nanoparticles. When approaching the Pt surface, the H$_2$ molecules will be dissociated into atomic H naturally. These H atoms can migrate across the Pt surface and even into the underlying carbon support. This effect is also known as the “spillover” effect$^{132,133}$. The H atoms can be removed via recombination into H$_2$ molecules and detached from the particle surfaces at a higher temperature.

In principle, the electrical conductivity of a material is related to the product of carrier concentration and carrier mobility, both of which play a key role in determining the conductance value of a gas sensor. The carrier concentration of a sensing material can be changed by accepting or donating carriers to adsorbed gas molecules, while the adsorbed gas molecules would also act as scattering centers for the carrier propagation, leading to decreased mobility. The conductance gas sensor works by bridging the two electrodes (source and drain) with sensing materials and passing current through them. Gas
detection can be realized by monitoring the current change upon exposure to the target gas environment under a constant voltage. For conductance-type gas sensors, both high sensitivity and fast recovery rate are desirable. However, these two criteria contradict each other to certain extent. High sensitivity demands a strong interaction strength between the gas molecules and the sensing system in terms of the charge transfer between them or the binding energy of gas molecules, and a strong interaction strength typically leads to a slow detachment rate of gas molecules from the sensing system. In other words, high sensitivity and quick recovery cannot be realized on the same system and the former is generally achieved at the price of the latter. Thus, it is desirable to design novel gas sensors that can circumvent this dilemma.

1.3.2 Quantitative Characterization of Sensitivity

The sensitivity of a sensing material is directly described by the ratio of conductance change before and after the gas adsorption to its conductance in the absence of target gases. Indirectly or fundamentally, however, the sensitivity is dictated by the intercorrelated quantities of interaction strength (i.e., between the gas molecules and the sensing materials) and the adsorption density or coverage. The stronger the interaction, the more gas molecules will be adsorbed (i.e., higher adsorption density or coverage). Consequently, sensitivity can be effectively enhanced either by increasing the target gas concentration or by strengthening the gas-surface interactions.

In principle, gas molecules could interact with solid surfaces via either the van der Waals attraction or by a chemical reaction. Although both would vary the conductance of the
solid, the van der Waals interaction could be used for the gas sensing applications, while the chemical reaction would be more suitable for catalysis. Upon the adsorption of gas molecules, the electronic structure of the sensing material will be altered and thus its conductance will change. For physical adsorption, the electronic structure is modified in such a way that only the Fermi level is tuned and the band dispersions remain invariant, i.e., the carrier mobility is unchanged. For example, graphene can be n-type or p-type doped with the Dirac cone intact through the charge transfer, depending on whether the gas species is reducing or oxidizing. Given that the conductivity is linearly proportional to the product of carrier concentration and mobility, its variation originates dominantly from the change of carrier concentration correlated with the amount of adsorbed gas molecules for gas sensing. However, the recovery rate would be quite slow (i.e., the adsorbed gas molecules are slow to detach from the sensing material) if the sensitivity is enhanced by increasing the interaction strength. For example, with the surface oxidized silver-based gas sensor, the response and recovery times toward 1% NH₃ and 1,250 ppm NO₂ detections are ~150 s and ~200 s, ~100 s and ~1,200 s, respectively. The prominent difference in the recovery time arises from the stronger interaction strength between the NO₂ and the oxidized silver surface by forming the NO₃ complex. To overcome this barrier and obtain the high sensitivity and fast recovery simultaneously, judicious routes include searching for new material whose conductivity is ultrasensitive to external perturbations, in which case only weak gas adsorption is necessary (e.g., graphene is ultrasensitive to NO₂ molecules and even a single molecule), and accelerating the gas desorption by a gate voltage or ultraviolet light irradiation, since both can effectively lower the energy barrier for gas molecules to
detach. In either circumstance, it is desirable as the starting point to characterize the gas adsorption both qualitatively and quantitatively in order to identify potential candidates for gas sensing and to tailor their performance.

Currently, however, the theoretical methodology to predict gas adsorption is in terms of the adsorption site, binding energy, and charge transfer. Gas molecules tend to be adsorbed on the sites with higher binding energies. The current consensus is that a higher binding energy (i.e., more charge transfer) favors a higher sensitivity. But the binding energy only provides the evidence of the qualitative ground and cannot provide further insight into how the gas sensitivity is intimately related to the binding energy in a more specific way that is suitable for gas sensing modeling. Quantitatively, both Touzik et al.\textsuperscript{137} and Lin et al.\textsuperscript{138} studied the gas adsorption capacity on graphitic surfaces. Their approaches require cumbersome procedures of fitting the gas-surface interaction potential predicted by the \textit{ab initio} calculations and solving the Schrödinger equation analytically. Practically, it would be encouraging to characterize the adsorption capacity more conveniently, with multiple benefits. On one hand, an easy approach facilitates the evaluation of the gas adsorption capability of various materials by circumventing the cumbersome procedures described above and helps the performance tuning of gas sensors in a controllable fashion; on the other hand, the derived simple-to-use expression for gas adsorption capacity can be integrated into the conductivity model for a specific material (e.g., CNTs\textsuperscript{139}, graphene\textsuperscript{140} and its nanoribbons\textsuperscript{141}) to faithfully represent the gas-surface interactions, establishing the model that gas sensing can be fundamentally understood in a multifunctional way so that even the concentration of target gases can be detected as opposed to identifying the presence of gas species only; finally, the approach can also be
applied beyond gas sensing and tapped into the fields such as gas storage or even surface catalytic reactions under certain conditions.

In summary, the conductance-based gas sensors can detect the presence of gas molecules by measuring the system resistance change upon gas adsorption. The resistance change is correlated with both carrier concentration and mobility variations of the sensing material in a proportional and an inversely proportional manner, respectively. Sensitivity and recovery rate are two major aspects in judging the performance of a gas sensor, but contradict with each other in principle in terms of the binding energies of gas molecules: the larger the binding energy, the higher the sensitivity and the slower the recovery. It is also possible to produce an insensitive gas sensor when the effects of carrier concentration and carrier mobility cancel each other. Therefore, it is of great significance to quantify changes in these two individual physical variables to inspire novel designs of sensing platforms.

1.4 Objectives of the Dissertation Research

As reviewed in previous sections, pure graphene is a semimetal and GO is nonstoichiometric and insulating. The newly discovered crystalline GMO is predicted to be semiconducting and can bridge the gap between graphene and GO. Moreover, nanoscale materials have attracted greater attention for gas sensor applications and fundamental understanding on their working principle is desirable. The overall objective of the current dissertation research is to explore the electronic properties and sensing performance of emerging 2D nanomaterials such as GMO, RGO, and BP through first-principles models and experiments.
For GMO, we focus on the following aspects: (1) Although vibrational spectroscopy can be a practical approach to help identify and characterize GMO, the current GMO synthesis produces a composite of GMO and RGO. Therefore, it is important to understand how these frequencies evolve under different conditions in order to use infrared (IR) as a characterization tool. To facilitate its experimental identification, the vibrational properties of GMO are simulated. (2) Among various efforts devoted to identifying potential mechanisms for generating band gaps in graphene and related materials, few can be used to tune the band gap over a wide range on the same device. GMO has a higher oxygen to carbon ratio (O:C=1:1) than the insulating GO and it is predicted to be semiconducting. Density functional theory (DFT) will be used to explore the interplay between the mechanical and electronic properties of pure GMO and its one-dimensional interface with graphene. (3) It has been predicted that GMO is able to switch between an indirect and a direct bandgap semiconductor using a tensile uniaxial strain along the zigzag direction. These (tunable) electronic properties make GMO quite appealing, but its potential for miniaturized electronics applications requires understanding its ability to dissipate heat. Density functional perturbation theory (DFPT) will be used to investigate the intrinsic thermal conductivity of monolayer GMO due to phonons. (4) Near the interface between GMO and graphene, it is also interesting to study the spin distributions due to epoxy pairs and compare them with counterparts of single epoxies using the spin polarized DFT calculations. This will open new avenues for tuning the magnetic properties of graphene-based materials and pave the way for potential spintronics applications.
To understand the mechanism of conductance-based gas sensors, we will carry out the following research: (1) We will investigate the gas adsorption capability on solid surfaces in terms of the gas adsorption density. In general, the sensor surfaces can be categorized into two types: a mobile adsorption surface upon which gas molecules can move across the solid surface with a very low energy barrier and a localized adsorption surface on which gas molecules prefer to be tightly bound to certain sites and remain almost stationary. A statistical thermodynamics modeling is developed to determine the gas adsorption density with gas molecule binding energy from the DFT calculation as the only input. Then, we compare the predicted adsorption density on graphene from our modeling with the experimental data. (2) The analytical modeling is established with inputs from the DFT calculations to interpret the experimentally observed thickness-dependent sensitivity of BP thin films. The modeling is composed two parts: the first part is more related to the variation of the band gap of BP with respect to the film thickness in the thin film region; the second part focuses on the effective film thickness, since the band gap is almost constant for sufficiently thick films. (3) Experimentally, the TRGO thin films obtained at different temperatures are characterized as a sensing platform, and the sheet resistance, carrier concentration, and carrier mobility before and after exposure to specific gases can be obtained through van der Pauw and Hall measurements. Moreover, the Raman spectra simulation and DFT calculations of gas adsorption are used to explain the experimentally observed unusual behavior of BP thin film sensors after surface oxidation. Finally, the carrier concentration and the carrier mobility before and after exposure to specific gases are obtained through I-V and FET measurements.
The remainder of this thesis is organized as follows: Chapter 2 describes the methods used in this research. Chapters 3-6 are the core of the dissertation research, focusing on the prediction of various properties of GMO (Chapters 3 and 4), quantitative modeling of gas adsorption density on RGO-based materials (Chapter 5), and prediction of sensitivity of the BP thin films and understanding its sensing behavior (Chapter 6). The conclusions and future research directions are summarized in Chapter 7.
CHAPTER 2 THEORETICAL AND EXPERIMENTAL METHODS FOR NANOMATERIALS CHARACTERIZATION

2.1 Density Functional Theory

In principle, the properties of any system (e.g., atoms, molecules, and solids) can be determined by solving the Schrödinger equation. Unlike a single-electron system, a many-body system features Coulomb interactions among the nuclei and electrons and their mutual interactions. The solutions to the wavefunctions must be properly antisymmetrized to satisfy the Pauli exclusion principle, from which the properties of the system can be obtained. However, it is very hard or even impossible to analytically solve the Schrödinger equation for such systems. In 1964, Hohenberg and Kohn proved two theorems\textsuperscript{142};

1. The external potential $V_{\text{ext}}(r)$ of a many-body system is uniquely determined by the ground state particle density $n_0(r)$ except for a constant.

2. A universal functional of the energy $E[n]$ can be defined to search for the ground state energy which corresponds with the ground state particle density $n_0(r)$, namely, $E[n(r)] \geq E[n_0(r)]$.

The Hohenberg and Kohn theorems lead to the fundamental statement of DFT that all ground state properties of a system can be faithfully determined by its ground state
particle density $n_0(r)$. In other words, the system properties can be obtained without knowing the exact numerical form of the external potential $V_{\text{ext}}(r)$. Thus, Kohn and Sham further proposed the ansatz that the ground state properties of a many-body system can be represented by the numerically soluble non-interacting system with all the many-body terms incorporated into a so-called exchange-correlation functional of the density$^{143}$.

The energy functional $E[n]$ contains the kinetic energy $T[n]$, interaction with the external potential $V_{\text{ext}}[n] = \int V_{\text{ext}}(r)n(r)dr$, and the electron-electron Coulomb interactions $V_{ee}[n]$. Based on the Kohn-Sham ansatz, the kinetic energy of an N-electron system $T_{KS}[n]$ can be approximated by the N-electron non-interacting system,

$$T_{KS}[n] = -\frac{1}{2} \sum_i^N <\phi_i|\nabla^2|\phi_i> \quad (2.1)$$

where $\phi_i$ is the wavefunction orbital. And the electron density $n(r)$ can be constructed from the orbitals $n(r) = \sum_i^N |\phi_i|^2$. The electron-electron Coulomb interaction $V_{ee}[n]$ is composed of two terms: the Hartree term $V_H[n] = 1/2 \int n(r_1)n(r_2)/|r_1 - r_2|dr_1 dr_2$ and the exchange-correlation term $V_{XC}[n] = (T[n] - T_{KS}[n]) + (V_{ee}[n] - V_H[n])$ which includes the errors from the approximations of non-interacting kinetic energy and the classical treatment of Coulomb interactions. By solving the Schrödinger equation numerically, the ground state electron density $n_0(r)$ can be achieved through self-consistently modifying the guess electron density $n(r)$.

The accuracy of the DFT calculations now comes down to three aspects: how the wavefunctions of electrons are expanded in a basis set, how the core electrons are treated,
and how the electron-electron exchange-correlation term is approximated. For the basis set, one can choose the atomic orbitals, Gaussians, and plane waves. The electron wavefunctions can be constructed by the projector atomic orbitals\textsuperscript{144}, muffin tin orbitals\textsuperscript{145}, augmented plane waves\textsuperscript{146} and linearized augmented plane waves\textsuperscript{147}. Since core electrons are tightly bound to the nucleus, the core states of individual atoms remain almost unchanged when forming molecules or solids. Therefore, the properties of matter are dictated by the valence electrons and the wavefunctions of core electrons can be reasonably smoothed for the sake of numerical simplicity. Since the smoothed wavefunctions are not faithful to core electrons, they are termed as pseudopotentials. The pseudopotentials currently used include orthogonalized plane waves\textsuperscript{148}, projector augmented waves\textsuperscript{149}, ultrasoft pseudopotentials\textsuperscript{150} and norm conserving pseudopotentials\textsuperscript{151}. Apart from the pseudopotentials, full potential is also adopted widely for more accurate predictions, especially for heavy atoms\textsuperscript{152}. As the electron-electron exchange-correlation interactions approximate the many-body effect, the judicious choice of the approximation depends on the system to be studied. For close-packed solids like face-centered cubic metals, the electrons can be viewed as homogeneous electron gas and local density approximation (LDA) mostly in the formalism of Perdew-Zunger (PZ)\textsuperscript{153} is successful for such systems. For other solids, the exchange-correlation energy is nonlocally determined and the gradient of electron density has to be considered. Thus, the generalized gradient approximation (GGA)\textsuperscript{154} in the formalism of Perdew-Burke-Ernzerhof (PBE)\textsuperscript{155} or Perdew-Yang (PW91)\textsuperscript{156} is a good choice for these systems. For molecules, the formalism of Becke-Lee-Yang-Parr (BLYP)\textsuperscript{157,158} is preferred in GGA.
DFT is now an ever-increasingly and widely used approach to study the ground state electronic properties of both solids and molecules due to its great predictive power and high accuracy. It can be used to understand the properties of matter and design new materials with desired properties for electronics, spintronics, and catalysis. It can also be used to investigate situations that are hard or impossible to study experimentally. Now with the progress of parallel computation, the modeling system in DFT calculations can be extended to hundreds or even thousands of atoms. However, it should be kept in mind that DFT fails in treating the strongly-correlated systems and the van der Waals interactions.

### 2.2 Density Functional Perturbation Theory

In the DFT calculations, the total energy can be obtained by solving the Kohn-Sham equations self-consistently with the potential or system fixed. However, many physical properties of a system also correlate with its response to the external perturbations, which could change the system. These perturbations could come from atomic displacements due to the thermal excitations, the contraction or dilation of the primitive cell of the system, and the homogeneous external electric or magnetic field. To investigate the effects of these perturbations on the properties of a system, it is necessary to consider the perturbations on the DFT platform.

DFPT is a powerful technique that treats such perturbations within the framework of DFT by adding some perturbing potentials. The system properties can be predicted from the DFPT calculations by taking different orders of the total energy, which includes both the
electronic part and nuclei-nuclei interactions with respect to the perturbations. For example, force, stress, and dipole moment can be determined from the the 1st order derivatives\textsuperscript{162}; strains, elastic constants, dielectric susceptibility, Born effective charge tensors and dynamical matrix can be determined from the 2nd order derivatives\textsuperscript{163}; nonlinear dielectric susceptibility, phonon-phonon interactions and Gruneisen parameters can be determined by the 3rd order derivatives\textsuperscript{163}. Thus, DFPT calculations have been used to predict a wealth of information for various systems\textsuperscript{164}, such as dielectric, piezoelectric, and elastic properties, phonons in crystals, alloys or at surfaces, interfaces of superlattices or nanostructures, Raman and infrared activities, structural phase transitions, electron-phonon interactions in the superconductor, thermal expansion, and lattice thermal conductivity.

In the phonon calculations, the perturbing potential is the displacement of a group of atoms. Assuming the variable $\zeta_{\lambda}$ depends on the parameter $\lambda$,

$$
\zeta_{\lambda}(r) \equiv \zeta(r) + \lambda \frac{\partial \zeta(r)}{\partial \lambda} + \frac{1}{2} \lambda^2 \frac{\partial^2 \zeta(r)}{\partial \lambda^2} + \cdots
$$

(2.2)

in which $\zeta_{\lambda}$ can be the external potential $V_{\lambda}(r)$, the charge density $n_{\lambda}(r)$, and the functional energy $E_{\lambda}$. Based on the Hellmann-Feynmann theorem, the 1st order derivative of energy $\partial E/\partial \lambda$ is free of any derivative of charge density $n(r)$\textsuperscript{162},

$$
\frac{\partial E}{\partial \lambda} = \int n(r) \frac{\partial V(r)}{\partial \lambda} \, dr .
$$

(2.3)

The 2nd order derivative $\partial^2 E/\partial \lambda^2$ is related to the 1st order derivative of charge density $\partial n(r)/\partial \lambda$\textsuperscript{163},

\[ \frac{\partial^2 E}{\partial \lambda^2} \]
\[ \frac{\partial^2 E}{\partial \lambda^2} = \int \frac{\partial V(r)}{\partial \lambda} \, \frac{\partial n(r)}{\partial \lambda} \, dr + \int n(r) \frac{\partial^2 V(r)}{\partial \lambda^2} \, dr. \]  

(2.4)

Owing to the variational character, the \((2n+1)^{th}\) order derivative of energy generally depends on only up to the \(n^{th}\) order derivative of charge density, and this is the \(2n+1\) theorem. Within the harmonic approximation, the central equation of phonons is\(^\text{164}\)

\[ \sum_{I,J} (C^\alpha_{I,J} - M_I \omega^2 \delta_{I,J} \delta_{\alpha\beta}) U^\beta_J = 0, \]  

(2.5)

where \(\alpha (\beta)\) is the cartesian component of atom \(I (J)\), \(U\) stands for the displacement pattern, \(\omega\) is the normal mode frequency, \(M\) is the atomic mass and \(C\) is the matrix of inter atomic force constants, which is defined as the \(2^{nd}\) order derivative of energy with respect to atomic positions \(R\),

\[ C^\alpha_{I,J} = \frac{\partial^2 E(R)}{\partial R_I^\alpha \partial R_J^\beta}. \]  

(2.6)

The frequency and displacement patterns also correlate with the wave vector \(q\) for crystals. And the Fourier transform of \(C^\alpha_{I,J}\) at arbitrary \(q\) is

\[ \tilde{C}^{\alpha\beta}_{st}(q) \equiv \frac{1}{N_C} \frac{\partial^2 E}{\partial \mu_s^{a}(q) \partial \mu_t^{b}(q)}, \]  

(2.7)

with \(N_C\) as the number of unit cells in the crystal. In polar materials, due to the partially ionic nature of covalent bond, the positively and negatively charged planes created by the longitudinal optical (LO) phonons along certain directions experience additional restoring force, which is now long-ranged in the real space and cannot be treated periodically. At
\( q = 0 \), if the LO and transverse optical (TO) phonons are degenerate, the degeneracy will be lifted by this restoring force. The dynamical matrix is split into an analytic term and a non-analytic term\(^{160}\):

\[
\tilde{C}_{s\alpha,t\beta}(q \to 0) = \tilde{C}_{s\alpha,t\beta}(q = 0) + \tilde{C}_{s\alpha,t\beta}^{NA}(q \to 0),
\]  
(2.8)

where

\[
\tilde{C}_{s\alpha,t\beta}^{NA}(q \to 0) = \frac{4\pi (q Z_s^\ast)_{\alpha}(q Z_t^\ast)_{\beta}}{\Omega_0 \sum_{\alpha\beta} q \varepsilon_{\alpha\beta} q_{\alpha\beta}}.
\]  
(2.9)

and the effective charge

\[
Z_s^{\ast\alpha\beta} = Z_s \delta_{\alpha\beta} - \frac{1}{N_e} \frac{\partial^2 E}{\partial \mu_s (q=0)}.
\]  
(2.10)

The infrared intensities can be obtained as\(^{164}\)

\[
I_{IR}(\nu) = \sum_{\alpha} |\sum_{s\beta} Z_s^{\ast\alpha\beta} U_s^{\beta}(\nu)|^2,
\]  
(2.11)

in which \( \nu \) is the frequency of infrared active normal mode.

### 2.3 van der Pauw and Hall Measurements

The van der Pauw and Hall method\(^{165,166}\) is a widely used technique to measure the sheet resistance and Hall voltage of 2D thin films, from which the type of carrier and its concentration and mobility can be determined. In our experiments, van der Pauw measurements are used to quantify the change in the carrier concentration and the mobility of the gas sensing material before and after its exposure to target gases. An
aluminum box is used to house the sample and to shield the sample from the surrounding electromagnetic disturbances.

Fig. 2.1. Schematic experimental setup for van der Pauw and Hall measurements: (a) exterior connections; (b) and (c) are top and side views inside the chamber, respectively.

Fig. 2.1 shows a schematic diagram of the experimental setup. The sample chamber (box) is sealed in a way that once the chamber is filled with target gas through the gas inlet, the concentration of the gas inside the chamber can be held nearly constant. There is a pair of jacks on each of the four sidewalls. For low noise measurements, BNC jacks are used. The sample is mounted on the bottom stage of the aluminum box with a piece of double-sided carbon tape. The tips of the copper wires (shown in red in Fig. 2.1 (b) and (c)) are connected to the inner part of the jacks with copper alligator clips. For Hall measurements, a permanent magnet (6,451Gauss) is located underneath the sample and
outside of the chamber (Fig. 2.1(c)), providing a magnetic field perpendicular to the sample surface.

Practically, the following conditions must be satisfied to obtain faithful results: (1) the thickness of thin film should be uniform and much smaller than its lateral size; (2) the material to measure should be unipolar and isotropic, and films should be prepared homogeneously with no isolated holes; (3) the electrodes must have an Ohmic contact with the sample and the occupied area is negligible compared with the sample surface area. In principle, this technique can be applied to samples with arbitrary shapes. However, for accurate measurements, square or rectangular samples with electrodes placed on their four corners are recommended to maximally avoid the discrepancy induced by the geometrical arbitrariness. The van der Pauw method contains two procedures, the sheet resistance and Hall voltage measurements. Here, the square-shaped sample is used as an example. Before the measurement, the electrodes can be labeled either clockwise or counterclockwise from one to four. The resistance of the sample should be estimated using a multimeter for the first few trial measurements with a low current. In that case, we can choose an appropriate current magnitude so that the Joule heating is small enough (P<0.1 W) without losing high-accuracy measurement.

In the resistance measurements, the current $I_{12}$ is defined as the current flow vertically across one edge (from electrode 1 to electrode 2) and the voltage $V_{43}$ (from electrode 4 to electrode 3) is measured at the opposite edge. The resulting vertical resistance $R_{12,43}=V_{43}/I_{12}$ can be obtained based on the Ohm’s law. In a similar manner, we can get the
horizontal resistance $R_{14,23} = V_{23}/I_{14}$. The sheet resistance for the thin film can then be determined by the following equation,

$$\exp(-\pi R_{12,43}/R_s) + \exp(-\pi R_{14,23}/R_s) = 1$$ (2.12).

To enhance the accuracy by cancelling any offset voltages using the reciprocity theorem ($R_{AB,CD} = R_{CD,AB}$) and reversed polarity measurements ($R_{AB,CD} = R_{BA,DC}$), the averaged vertical and horizontal resistances are

$$R_v = (R_{12,43} + R_{21,34} + R_{43,12} + R_{34,21})/4$$ (2.13a)

and

$$R_h = (R_{14,23} + R_{41,32} + R_{23,14} + R_{32,41})/4$$ (2.13b),

respectively. Thus, the sheet resistance can be obtained by modifying Eqn. (2.21) into

$$\exp(-\pi R_v/R_s) + \exp(-\pi R_h/R_s) = 1$$ (2.14).

Practically, the measurement accuracy can be trusted only when the relative errors of each pair of reciprocal and reversed measurements are within 3%. Otherwise, sources of error from either the experimental setup or the sample preparation should be identified.

In the Hall voltage measurement, the current and the voltage in the presence of an external magnetic field are measured instead across the corners of the sample. For example, if the magnetic field along the $+z$ direction is assigned as positive (P), the Hall voltage $V_{13P}$ between the electrodes 1 and 3 is developed when current $I_{42}$ is applied.
from electrodes 4 to 2. We can also obtain Hall voltage $V_{13N}$ with the magnetic field flipped. Thus, the Hall voltage is

$$V_{13}=(V_{13,24,P} - V_{13,24,N})/2 \quad (2.14a).$$

Similar to the resistance measurement, by reciprocal and reversed polarity measurements, other sets of Hall voltages are

$$V_{31}=(V_{31,42,P} - V_{31,42,N})/2 \quad (2.14b),$$

$$V_{24}=(V_{24,31,P} - V_{24,31,N})/2 \quad (2.14c),$$

$$V_{42}=(V_{42,13,P} - V_{42,13,N})/2 \quad (2.14d).$$

And the average Hall voltage is

$$V_H=(V_{13}+V_{31}+V_{24}+V_{42})/8 \quad (2.15),$$

the sign of which indicates the type of carriers, namely, positive for holes and negative for electrons. Then, the sheet carrier density is calculated as

$$n_s=IB/|e|V_H \quad (2.16),$$

where I and B are the current and the magnetic field, respectively. We can obtain the carrier Hall mobility using the following expression

$$\mu_H=(|e| n_s R_s)^{-1} \quad (2.17).$$
2.4 Field-Effect Carrier Mobility Measurements

![Schematics of FET in the dual-gate geometry for field mobility measurements.](image)

Fig. 2.2 Schematics of FET in the dual-gate geometry for field mobility measurements. (a) Upper panel: the top view of the six probe configuration, lower panel: the cross-sectional view of a typical double-gated FET; (b) The transfer characteristics of an n-type semiconductor, with the linear region indicated by the red dashed line. The intercept with respect to the gate voltage is the extrapolated threshold gate voltage \( V_{th} \).

Carrier mobility is an important parameter for FET-based devices because it determines the power dissipation and switching speed. Fig. 2.2 (a) shows a comprehensive FET device with the source/drain electrodes in the six-probe configuration (enabling the two/four-terminal and Hall measurements) and the dielectric media in the double-gated geometry. In the linear regime of the transfer characteristics (Fig. 2.2 (b)) where the
carrier concentration is controlled by the capacitive coupling to a gate, the effective mobility $\mu_{\text{FE}}$ is

$$\mu_{\text{FE}} = \frac{L}{W} \frac{g_m}{CV_{DS}}, \quad g_m = \frac{dI_{DS}}{dV_{BG}}$$

(2.18)

where $g_m$ is the transconductance, $V_{BG}$ is the back gate voltage, $V_{DS}$ ($I_{DS}$) is the drain voltage (current), $L$ ($W$) is the channel length (width), and $C$ is the gate-channel capacitance. $C$ can be either calculated from the parallel-plate capacitance model or extracted by the Hall measurement. In the parallel-plate model, $C = \varepsilon_0 \varepsilon_r / d$, where $\varepsilon_0$ and $\varepsilon_r$ are the permittivity of vacuum and back gate oxide ($\varepsilon_0 = 1$ and $\varepsilon_r = 3.9$ for SiO$_2$), respectively, and $d$ is the thickness of the back-gate oxide. In the Hall measurement, the carrier density $n$ is determined as $n(V_{BG}) = B/e\rho_{23}(V_{BG}, B)$, where $B$ is the applied magnetic field, $\rho_{23} = V_{23} W / I_{DS} L$ is the sheet resistivity. The gate capacitance can then be calculated as $C = n(V_{BG}) e/(V_{BG} - V_{\text{th}})$, where $V_{\text{th}}$ is the threshold gate voltage. Mostly, the capacitance is calculated using the serial capacitor model since it is close to the value extracted from the Hall measurement that is more accurate$^8$.

Generally, the contact resistance from the Schottky barrier at the interface would result in the underestimation of carrier mobility in a two-terminal configuration (source-drain voltage and current) compared with the value obtained in a four-terminal configuration (in which $I_{DS}$ is replaced by $I_{12}$). For example, the intrinsic carrier mobility of multilayer MoS$_2$ is 91 cm$^2$/V·s in the two-terminal configuration measurement, much smaller than 306.5 cm$^2$/V·s extracted from the same device in a four-terminal configuration$^{167}$. 

It has also been shown that the mobility degradation in the 2D thin films-based field-effect devices mainly results from the trapped charges in the substrate whose Coulomb potential will penetrate into the thin films and lead to the carrier localization\textsuperscript{168}. Physically, both the Coulomb and surface roughness scattering will have a negative impact on the carrier mobility in the nanoscale membranes, as the substrate (including the overlayer of a thin-film transistor) and the surface impurities will introduce either the long-range charge disorder or the short-range disorder caused by chemical bonding or roughness\textsuperscript{169}. Thus, considerable improvements on carrier mobilities in these nanoscale membranes require the screening of both the substrate and impurities scattering through proper design of the dielectric environment.

Technically, the strong suppression of charged-impurity scattering can be realized either by coating the nanostructures with high-\(\kappa\) dielectrics overlayer or in the dual-gate devices with a top-gate high-\(\kappa\) dielectric, leading to as much as one order of magnitude enhancement in carrier mobilities for thin 2D semiconductor membranes and even more for semiconductor nanowires\textsuperscript{170}. For example, the room-temperature single-layer MoS\(_2\) mobility is at least 200 cm\(^2\) V\(^{-1}\) s\(^{-1}\) extracted from the FET measurement with a halfnium oxide top gate dielectric\textsuperscript{171}, almost two orders of magnitude larger than the reported mobilities in the 0.5–3 cm\(^2\) V\(^{-1}\) s\(^{-1}\) range without the top gate\textsuperscript{88}. In addition, Jang \textit{et. al} showed that adding a water overlayer on graphene in ultrahigh vacuum (i.e., the background dielectric constant enhancement) will reduce the interaction strength of electrons with charged impurities and thereby increase (decrease) the dielectric screening (impurities scattering)\textsuperscript{169}. As a result, the mobility increased by more than 30\%. Note that the Coulombic scattering in membranes only below a critical thickness can be strongly
suppressed by coating the semiconductor layer with insulating dielectric barriers with a high dielectric constant because the screening of scattering will be much weaker beyond this critical thickness\textsuperscript{170,172}. Another route to enhance the carrier mobility is to improve the surface quality of the substrate. The charge carrier mobility of multilayer MoS\textsubscript{2} on polymethyl methacrylate extracted from the FETs in a four-probe configuration by Bao \textit{et al.} is up to 470 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1}, a significant improvement compared with the mobility of 30–60 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1} on SiO\textsubscript{2}\textsuperscript{173}.

It is still under debate that the mobility enhancement is ascribed to the damping of Coulombic scattering. Xia \textit{et al.} carried out the Hall measurement on the back-gated graphene FETs with and without a top dielectric medium, which showed that the back-gate capacitance is enhanced dramatically by the high $\kappa$ top dielectric medium and this enhancement increases with the size of the top dielectric medium, but the mobility does not change significantly. Hence, they strongly suggested that the top dielectric medium-induced charge transport properties of graphene FETs arise from the increase of gate capacitance instead of enhancement of carrier mobility\textsuperscript{174}. Fuhrer and Hone\textsuperscript{90} also argued that the capacitive coupling between the back and top gates in the dual-gate devices (dependent on the top-gate pad size) can cause the back-gate capacitance to differ significantly from the value predicted by the parallel-plate model. Consequently, mobility overestimation by a factor of $C_{Tg}/C_{Bg}$ arises when neglecting this coupling. They further argued that measurements in the double-gated devices with well-defined capacitances would yield the mobility $\mu_{FE} = 2–7$ cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1}, similar to the mobility from the measurements in the back-gate devices. However, Radisavljevic and Kis\textsuperscript{89} performed the measurements with the accurate determination of both the contact resistance and the
capacitive coupling. They showed that the mobility is indeed significantly higher than the value without the top gate dielectric medium. Therefore, the mobility enhancement by the high $\kappa$ top dielectric deposition is still valid.
CHAPTER 3 GRAPHENE MONOXIDE: A NOVEL CARBON-BASED SEMICONDUCTING MATERIAL

In contrast to pure graphene that is a semimetal and GO that is nonstoichiometric and insulating, a new crystalline structure GMO, as experimentally observed through thermal reduction of multilayer GO inside a transmission electron microscopy (TEM) chamber, is predicted to be semiconducting and can bridge the gap between graphene and GO. In this chapter, various properties of GMO are explored. In Section 3.1, the IR characteristics of both pure GMO and GMO domains embedded in the graphene matrix are first investigated to help identify the GMO domains during the formation process, since GMO evolves from the thermal reduction of GO. In Sections 3.2 and 3.3, electronic and thermal properties of GMO are studied for future electronic applications, respectively.

3.1 Structural Identification from Infrared Bands

3.1.1 Infrared Properties of Monolayer GO Sheets

To calculate the IR properties of GMO, GO, and GMO-graphene composites, we use the plane wave pseudopotential Quantum Espresso package within the DFT and DFPT frameworks. The computational parameters include a wave function (charge density) cutoff of 40 Ry (480 Ry), LDA-PZ form of exchange-correlation, an 18×18×1 Monkhorst-Pack mesh for Brillouin zone sampling, and a vacuum region greater than 15 Å. The acoustic sum rule was imposed to guarantee the vanishing frequency value of acoustic modes at Γ. Although the absolute values of the calculated frequencies should
not be expected to be given precisely, differences and trends among them are generally more robust. As a validation of the overall expected accuracy, we have calculated (using the same computational parameters) the vibrational frequencies of graphene and carbon dioxide, and found that discrepancies with experimental values are no more than 50 cm⁻¹.

GO is essentially nonstoichiometric and the local coverage of oxygen-containing groups varies from C₁O₀.₅ to C₁O₀.₇₅⁴⁵,¹⁷⁷. Thus, it is impractical to establish a model that can truly represent the structure of GO; however, it is reasonable to adopt a structural representation that includes critical features of GO to predict the frequencies and intensities of vibrational excitations detected with infrared spectroscopy and compare the predicted data with experimental results. Both theoretical and experimental results on the distribution of functional groups indicate that epoxides and hydroxyls are mostly adjacent to each other (irrespective of the tiny domains of each species) and carbonyls (carboxyls) are located near the C vacancies (edges)¹⁷⁸,¹⁷⁹. Since the major functional groups in GO are epoxide and hydroxyl groups, only these groups are included in our IR simulations of GO. We employ the structural configuration (as shown in the inset of Fig. 3.1(a)) with two epoxides and two hydroxyls placed in close proximity on the C lattice of graphene in 3×3 unit cells, representing an O coverage of ~22%. Fig. 3.1(a) shows the predicted IR spectra for the GO model. For the grazing incidence (GI) spectrum, the aromatic C=C bonds are not excited and vibrations of epoxides and hydroxyls give rise to three broad
Fig. 3.1 (a) Theoretical IR spectra of GO in the GI (upper panel) and NI (lower panel) orientation. The inset shows the adopted schematic structure of unreduced GO. (b)
Atomic displacements of C=C vibration in the GO structure in (a) with frequencies of 1,350 cm$^{-1}$, 1,530 cm$^{-1}$ and 1,590 cm$^{-1}$. The pink arrows indicate the vibration vectors with the length of them proportional to forces.

peaks with central values of ~925 cm$^{-1}$ (C-O-C asymmetric stretching), ~1,020 cm$^{-1}$ (C-OH stretching), and ~1,325 cm$^{-1}$ (C-OH angle bending), respectively. For the normal incidence (NI) spectrum, there are four broad peaks with central values of ~1,050 cm$^{-1}$ (C-O-C symmetric stretching), ~1,250 cm$^{-1}$ (C-O-C asymmetric-like stretching coupled to both C=C bonds and C-OH), ~1,350 cm$^{-1}$ (C=C) and ~1,560 cm$^{-1}$ (C=C), respectively. The broad C=C peak around 1,560 cm$^{-1}$ actually contains two peaks located at ~1,530 cm$^{-1}$ and ~1,590 cm$^{-1}$. As seen in Fig. 3.1 (b), the atomic displacement of C=C mode at ~1,350 cm$^{-1}$ is also coupled with the C atoms in the epoxide, while those modes at ~1,560 cm$^{-1}$ arise mainly from the C=C stretching in graphene with similar dynamic dipole intensity but in different directions from the C displacements. The frequency differences (<70 cm$^{-1}$) between the theoretical predictions and the experimentally observed values could be due to the potential interactions among the functional groups with the intercalated water molecules other than theoretical uncertainty. Thus, the calculated spectra qualitatively agree well with the experimental observations shown in Fig. 3.1(a), which suggests that our model and theoretical methods are appropriate and successful.

3.1.2 Infrared Properties of GMO

Fig. 3.2 (a) presents the crystalline structure of GMO. The unit cell consists of four atoms with two C atoms bridged by an O atom both above and below the lattice plane. Opposed
to the honeycomb arrangement of $sp^2$ C atoms in graphene, C atoms in GMO are transformed to form four bonds with the neighboring two C and two O atoms, forming $sp^3$-like hybrid orbitals. Furthermore, the underlying C lattice is now distorted from the hexagonal lattice of graphene ($\alpha=120^\circ$) to a centered rectangular (quasi-hexagonal) lattice. For the fully relaxed structure, the lengths of the primitive lattice vectors are (cf., Fig. 3.2 (a)) $a=3.09$ Å and the angle between them is $\alpha=130.2^\circ$, with the C-C and C-O bond lengths of 1.54 Å and 1.38 Å, respectively.
Fig. 3.2 (a) Upper panel: perspective view of GMO in 3×3 unit cells with lattice vectors and angles defined; C and O atoms are represented by yellow and red balls, respectively. Lower panel: schematics of the three IR active normal modes with the corresponding symmetries labeled, and eigenvectors are indicated by arrows. (b) Calculated IR spectra of monolayer pristine GMO via convolution of frequency with Gaussian function for grazing (GI) and normal (NI) incidence. Black and blue lines represent the cases without and with LO-TO effect taken into account; symbols and numbers show the symmetry of the mode and its frequency peak value, respectively. The inset indicates the variation trend of frequency with regard to lattice angle.

Due to the quasi-hexagonal lattice, the point group of GMO has been lowered from $D_{6h}$ of graphene to $D_{2h}$. As there are 4 atoms in the unit cell of GMO, there are 12 phonon...
normal modes in total. To distinguish which mode is IR active, we need to determine the reducible representation \( \Gamma_{3n} \) first and then reduce it into the linear combinations of irreducible representations. To find out the character \( \chi_{R,i} \) of \( \Gamma_{3n} \) where \( i \) runs through all the symmetry operations, we count the numbers of atoms \( N_i \) in the unit cell that are left invariant after imposing the operation \( i \), and then multiply it by the contribution \( \chi_i \) from the nonshifted atoms (namely, \( \chi_{R,i} = N_i \chi_i \)). For the \( D_{2h} \) group, which is non-degenerate, \( \chi_i \) is equal to the sum of characters in operations \( B_{1u}, B_{2u}, B_{3u} \) in the character table which transform as the three unit vectors in the Cartesian coordinates \( x, y, z \). Then, for any group with finite order, we can achieve the reduction by using the equation

\[
n_i = \sum_c g_c \chi_{R,i} \chi_r / h,
\]

where \( n_i \) is the number of times that the irreducible representation \( i \) occurs in the reducible presentation \( \Gamma_{3n} \); \( c \) stands for the class in the group and \( g_c \) means the number of operations in the class \( c \); \( \chi_r \) is the character of irreducible representation corresponding with class \( c \) and \( h \) is the order of the group. For group \( D_{2h} \), \( g_c = 1 \) holds for all the classes and \( h \) is 8. Table 3.1 displays the complete worksheet showing the reduction of \( \Gamma_{3n} \). It can be seen that

\[
\Gamma_{3n} = 2A_g + B_{1g} + B_{2g} + 2B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}.
\]

By subtracting the three translation modes

\[
\Gamma_{\text{trans}} = B_{1u} + B_{2u} + B_{3u},
\]

we obtain 3n-3 vibrational modes \( \Gamma_{3n-3} = 2A_g + B_{1g} + B_{2g} + 2B_{3g} + B_{1u} + B_{2u} + B_{3u} \), where \( A_g \), \( B_{1g} \), \( B_{2g} \), \( B_{3g} \) are Raman active and \( B_{1u}, B_{2u}, B_{3u} \) are IR active. Therefore, 3(6) non-degenerate modes are IR (Raman) active of the 9 vibrational modes.
TABLE 3.1. Complete worksheet showing the reduction of $\Gamma_{3n}$ with the transformation properties of unit and rotational vectors included.

<table>
<thead>
<tr>
<th>$\chi_i$</th>
<th>$N_i$</th>
<th>$\Gamma_{3n}$</th>
<th>$\chi$</th>
<th>$n=\Sigma/h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_{2h}$</td>
<td>E</td>
<td>C$_{2x}$</td>
<td>C$_{2y}$</td>
<td>C$_{2z}$</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-3</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

The IR active vibrational modes, with displacements perpendicular to the film for one mode (B$_{1u}$) and displacements in plane for the other two modes (B$_{2u}$ and B$_{3u}$) are shown in the lower part of Fig. 3.2 (a). For all the IR active modes, the C and O atoms vibrate with atomic displacements opposite to each other, as expected in order to generate the dynamic dipoles needed to be IR active. Since the displacements of the B$_{1u}$ mode are perpendicular to the lattice plane (along the z axis) and those of B$_{2u}$ and B$_{3u}$ lie within the plane (along y and x axes, respectively), they should be distinguishable experimentally. Fig. 3.2 (b) shows the geometrically resolved IR activity of a free-standing monolayer GMO. Vibrational modes that produce a dynamical dipole moment within the plane of the crystal are detectable in a normal incidence (NI) transmission measurement, while those normal to the basal plane are detectable in a grazing incidence (GI) reflection-absorption measurement. The calculated frequencies of the normal modes are 1,011 cm$^{-1}$ (B$_{2u}$), 506 cm$^{-1}$ (B$_{3u}$), and 1,021 cm$^{-1}$ (B$_{1u}$), with relative peak intensities of 0.75 to 0.06 and 0.02, respectively. Because the point group of GMO, D$_{2h}$, is centrosymmetric, the
“rule of exclusion” is valid and there is no silent mode ($A_u$). Hence, the Raman spectrum could also be used to characterize the structure of GMO: the calculated Raman frequencies are $312 \text{ cm}^{-1}$ ($B_{2g}$), $699 \text{ cm}^{-1}$ ($B_{3g}$), $902 \text{ cm}^{-1}$ ($A_g$), $995 \text{ cm}^{-1}$ ($B_{3g}$), $1,114 \text{ cm}^{-1}$ ($B_{1g}$), and $1,320 \text{ cm}^{-1}$ ($A_g$).

Since GMO is a polar material, the long-range Coulomb interactions give rise to a macroscopic electric field that cannot be treated periodically. Thus, a non-analytical term is added to correct the frequencies of the LO-TO splittings\textsuperscript{164}, which blue-shifts the modes to $1,096 \text{ cm}^{-1}$ ($B_{2u}$), $523 \text{ cm}^{-1}$ ($B_{3u}$), and $1,025 \text{ cm}^{-1}$ ($B_{1u}$), with nearly equivalent intensities. (The shift of the $B_{1u}$ mode should be zero for an isolated GMO monolayer and the small/negligible shift demonstrates that the vacuum region in the calculations is thick enough.) The relatively large frequency shifts for the $B_{2u}$ and $B_{3u}$ modes suggest that the structural anisotropy of GMO plays an important role for the vibrations along the armchair ($B_{2u}$) and zigzag ($B_{3u}$) directions. As shown previously, the planar modulus for GMO along the armchair direction is about 150\% larger than that along the zigzag direction\textsuperscript{180,181}, and the frequencies of the $B_{2u}$ and $B_{3u}$ modes obey a similar relationship. Moreover, because GMO is much softer than graphene along the zigzag direction, we further consider the situation that GMO is stretched along this direction. The calculated IR frequencies with respect to angle (inset to Fig. 3.2 (b)) show that the $B_{2u}$ mode is largely unaffected, while the frequency of the $B_{1u}$ ($B_{3u}$) mode undergoes a red-shift (blue-shift) as the lattice angle increases. Therefore, atomic distortions along the armchair direction experience a larger restoring force.
Fig. 3.3. Calculated IR spectra for different structures. (a) GMO domains imbedded in the graphene matrix with and without single-epoxy at their interface, C\textsubscript{2}O domain in graphene and pure C\textsubscript{2}O layer from up to down, respectively; (b) 4 most energetically favored configurations with 3 single-epoxies decorated on both sides of graphene. The insets in (a) and (b) are the structures corresponding with each spectrum.

Previous IR experiments\textsuperscript{182} on putative as-prepared RGO/GMO composite materials revealed distinctive peaks in the normal and grazing incidence geometries in good agreement with the theoretical values for the B\textsubscript{1u} mode, but the predicted frequency of the
$B_{2u}$ mode (1,096 cm$^{-1}$) differs by approximately 100 cm$^{-1}$ from the observed experimental value (1,205 cm$^{-1}$). This discrepancy might be attributed to the fact that as-prepared GMO is buried within a multilayer RGO/GMO, giving rise to shifts compared with the isolated GMO monolayer.

As the unit cell planar area for GMO is ~20% larger than that of graphene, a GMO domain embedded into the graphene matrix is buckled to maximally release the strain due to the lattice mismatch. Here, we consider the situations both with and without single epoxide groups connecting graphene and GMO regions (cf., insets to Fig. 3.3 (a)). With the single epoxide groups, the predicted IR spectrum (top Fig. 3.3 (a)) of the ground state structure shows two major broad bands at 1,290 cm$^{-1}$ and 980 cm$^{-1}$, together with low intensity peaks at 1,486 cm$^{-1}$ and 662 cm$^{-1}$, respectively. When the single epoxide groups are removed, the ground state structure is still stable and does not evolve into carbonyl pairs$^{183}$. However, the predicted spectrum (middle Fig. 3.3 (a)) exhibits several changes: (i) the shoulder at 1,486 cm$^{-1}$ disappears; (ii) a red-shift by 12 cm$^{-1}$ occurs for the peak at 1,290 cm$^{-1}$; and (iii) the band at 980 cm$^{-1}$ narrows in the high frequency region (~1,200 – 1,150 cm$^{-1}$), with the shoulders within that region vanishing. The differences between these two spectra of GMO/graphene hybrid structures with and without epoxy groups at the interface suggest that epoxide-pairs in GMO contribute mainly to the two remaining bands at ~1,278 cm$^{-1}$ and 983 cm$^{-1}$, while the bands at ~1,486 cm$^{-1}$ and within the region from ~1,200 to 1,150 cm$^{-1}$ have more contributions from the single-epoxide groups. Since the GMO domain size (~1.5 nm$^2$) in the structural models in Fig. 3.3 (a) is small (for computational reasons) compared with the experimental situation, the interior of
GMO in our model is more strained, giving rise to the discrepancies (~70 cm⁻¹) between the predicted and the observed values.

Since the pathway to generate GMO is likely initiated by isolated single epoxide groups that coalesce – and the starting material is known to contain single epoxide groups – we consider how the IR spectrum develops for other structural configurations with only single-epoxide groups on the graphene, providing information about the spectral feature for the thermally-reduced GO to different degrees when hydroxyls are mainly detached but remnants of epoxides exist. We start with the crystalline structure with the lowest local C to O ratio 2:1 (C₂O), which is supported both experimentally and theoretically and can form via the migration of epoxides on the carbon plane under a high temperature. The infinitely large C₂O layer produces two IR active modes that are close to each other in frequency (980 cm⁻¹ and 904 cm⁻¹ in the bottom of Fig. 3.3 (a)) and would overlap in the spectrum due to inhomogeneous broadening. However, for a C₂O domain within a graphene matrix, coupling to the sp² C atoms leads to two more broad bands at 1,392 cm⁻¹ and 643 cm⁻¹. Therefore, the predicted spectra of this crystalline C₂O structure have no frequency overlaps with the bands from GMO.

Apart from the crystalline C₂O structure, small islands of epoxy species with amorphous configurations are also considered here to examine their spectral features since they are very likely to exist in RGO. Fig. 3.3 (b) shows the predicted spectra for the four most energetically favored configurations with three epoxies decorated on graphene. There are three common spectral regions with distinct absorptions: ~1,426–1,396 cm⁻¹, ~1,195–
1,163 cm\(^{-1}\), and ~861–806 cm\(^{-1}\), but none of these is consistent with the experimentally observed bands at 1,205 cm\(^{-1}\) and ~1,050 cm\(^{-1}\) for the RGO/GMO\(^{182}\) composite.

To simulate the impact on the normal mode frequencies due to the interactions between layers, we created a “bulk” GMO model similar to (multilayer) graphite. By fully relaxing the structure, we find that GMO prefers the graphitic AB stacking. Since van der Waals type interactions are not well described within normal DFT calculations, and the inter-layer spacing of multilayer GO after reduction varies from 3.4 to 6 Å\(^{185}\), we considered three different separations. The results are summarized in Fig. 3.4 (a). The frequencies vary only slightly compared with those of a monolayer GMO for all three modes when the layer separation is beyond 3.75 Å due to the much weaker layer interactions. However, the theoretical frequencies for B\(_{1u}\) and B\(_{2u}\) modes with an interlayer spacing of 3.5 Å are overestimated compared with the experimental observation, suggesting that the nominal layer spacing for bulk GMO is greater than 3.5 Å and the layer spacing of graphite (3.35 Å). When the layer spacing is varied between 3.75 and 4.0 Å, the theoretical frequency for the B\(_{1u}\) (B\(_{2u}\)) mode increases from 1,025 cm\(^{-1}\) (1,096 cm\(^{-1}\)) to ~1,034 cm\(^{-1}\) (1,170 cm\(^{-1}\)) due to the layer interactions. The predicted frequency of the B\(_{2u}\) mode for the multilayer is blue-shifted by ~75 cm\(^{-1}\) compared with that of the monolayer. The B\(_{3u}\) mode remains at 534 cm\(^{-1}\) for layer separations larger than 3.75 Å. The intensities, normalized to each layer, for the B\(_{1u}\) mode are predicted to increase significantly from 0.02 to 0.12, while the intensities of the other modes remain unchanged.
Fig. 3.4 Calculated IR frequencies of normal modes of GMO in two distinct stacking orders for different layer separations: (a) AB, (b) AB’. The insets in the upper panel in (a) and (b) are schematics of the stacking, and the intensity is normalized to each layer.
Given that GMO films are presumably randomly oriented in experiments (as evidenced by the rings in the diffraction results\textsuperscript{182}), we change the stacking from AB (in which the O atoms sit almost above the C atoms in the underlying layer) to AB’ (in which the oxygen atoms are now lined up and situated above the center of C rings in the underlying layer by shifting the B layer along the armchair direction). Compared with the AB stacking, the frequencies for both the B\textsubscript{1u} and B\textsubscript{2u} modes are blue-shifted by \(~20\) cm\textsuperscript{-1} and \(~40\) cm\textsuperscript{-1} for layer separation of 3.75Å. When the layer spacing is reduced (increased) to 3.50Å (4.0Å), however, the frequencies for the B\textsubscript{1u} and B\textsubscript{2u} modes are red-shifted (blue-shifted) by \(~50\) cm\textsuperscript{-1} (\(~15\) cm\textsuperscript{-1}) and \(~30\) cm\textsuperscript{-1} (\(~25\) cm\textsuperscript{-1}). In contrast to the AB stacking order, the frequencies for the B\textsubscript{3u} mode for the AB’ stacking order for all three layer distances are red-shifted, possibly due to the repulsion between neighboring O atoms along the zigzag direction reducing the restoring force. For separations between 3.75 and 4.0 Å, the calculated frequencies are now \(~1,051\) and \(~1,202\) cm\textsuperscript{-1} for the B\textsubscript{1u} and B\textsubscript{2u} modes, respectively, and fall into the experimentally observed frequency regions\textsuperscript{182}. Importantly, these frequencies are substantially red-shifted from the values calculated for the single epoxide groups of GO. In particular, the B\textsubscript{2u} mode (C-O-C asymmetric stretching) is shifted from 1,250 cm\textsuperscript{-1} in GO to 1,202 cm\textsuperscript{-1} in GMO. Note that the structural models in Fig. 3.4 (a) and (b) are two extreme situations, the experimentally broad IR bands of GMO come from combinations of its domains in the RGO matrix with varying stacking orders and layer distances.
Fig. 3.5. Evolution of the IR frequencies of the normal modes as a function of the number of layers of GMO in the (a-b) AB and (c-d) AB' stacking orders with layer distance fixed at 3.75 Å. (a) and (c): $B_{1u}$ mode (grazing incidence), (b) and (d): $B_{2u}$ and $B_{3u}$ modes (normal incidence).
Besides the potential interactions among GMO layers, interactions between GMO and graphene layers also could affect the frequencies of the GMO specific modes. To take this into account, a three-dimensional periodic supercell is constructed: a 4×4 GMO supercell is stretched along the zigzag direction so that the lattice angle is altered from 130° to 120°; and then a graphene 5×5 supercell is placed on top of a GMO layer with the layer separation fixed at 3.75 Å. For the stretched GMO monolayer, the calculated frequency for the $B_{1u}$ ($B_{2u}$) mode is 1,097 cm$^{-1}$ (1,082 cm$^{-1}$), while the $B_{3u}$ mode softens. After interaction with the graphene layer, the frequency for the $B_{1u}$ ($B_{2u}$) mode is red-shifted by about 10 cm$^{-1}$ (16 cm$^{-1}$). The slight red-shift is mainly due to the attraction between the C atoms in the graphene layer and the O atoms in the GMO layer. Nevertheless, the red-shift is quite small, especially for the $B_{2u}$ mode, compared with the blue-shift (~100 cm$^{-1}$) due to the interaction between the adjacent GMO layers.

The number of GMO layers could potentially be determined by considering the evolution of the frequencies of the IR modes, similar to the Raman technique used to judge the number of graphene layers. Since the predicted intensity of the $B_{1u}$ mode of GMO is much smaller than that of the $B_{2u}$ mode, separate grazing and normal incidence measurements will likely be needed experimentally. Fig. 3.5 shows the frequencies of GMO (with AB stacking) as a function of the number of layers. For the $B_{1u}$ mode in Fig. 3.5 (a), the slope is ~4 cm$^{-1}$/layer up to five layers, and then the frequency remains unchanged for more layers. However, the intensity continues to increase as a function of additional layers. Since the intensity of $B_{3u}$ is much smaller than that of the $B_{2u}$ mode (as well as its small frequency shift), it is not a strong indicator of the number of layers. The strongest changes as a function of the number of layers of GMO are predicted for the $B_{2u}$
mode, as shown in Fig. 3.5 (b): the frequency experiences a relatively large blue shift of ~12 cm\(^{-1}\) / layer up to five layers, which decreases to ~ 6 cm\(^{-1}\) / layer for five to nine layers. Above ten layers, the frequency increases extremely slowly. We also examined the case for GMO stacked in the AB' order as shown in Fig. 3.5 (c) and (d), and we can see that the trends are quite similar to GMO in the AB stacking order except the predicted slopes of frequency shift are slightly different. For example, the B\(_{1u}\) mode experiences the frequency shift of ~ 5 cm\(^{-1}\) up to 5 layers, while the slope for B\(_{2u}\) mode is ~7 cm\(^{-1}\) up to 7 layers. For both modes, the frequency increase slows when the number of layers increases. Hence, IR intensities can be used as a tool to identify the number of pure GMO layers for up to a ten-layer thick GMO, mainly by inspecting the frequency shift of the B\(_{2u}\) mode in normal incidence and the B\(_{1u}\) mode in grazing incidence.

In summary, we have calculated the vibrational properties of graphene oxide and GMO. GO primarily shows four bands around 1,560 cm\(^{-1}\) due to sp\(^2\) carbons, 1,350 cm\(^{-1}\) due to the angle bending of hydroxyl, 1,250 cm\(^{-1}\) due to the asymmetric stretching of epoxide,
and 1,050 cm\(^{-1}\) due to the symmetric stretching of epoxide and stretching of hydroxyl. For GMO as summarized in Table 2, among the three infrared active modes, the \(B_{2u}\) and \(B_{3u}\) modes (\(B_{1u}\) mode) can be observed in the N(G)I with frequencies of \(~1,096\) cm\(^{-1}\) and \(~523\) cm\(^{-1}\) (\(~1,025\) cm\(^{-1}\)) for a monolayer GMO, although the intensities of the \(B_{1u}\) and \(B_{3u}\) modes are much smaller than that of the \(B_{2u}\) mode. For GMO domains grown in a graphene matrix, the edges are mostly strained, resulting in large band shifts. Since GMO is soft along the zigzag direction, we also have shown that the frequency of the \(B_{3u}\) mode exhibits a moderate shift for a tensile strain applied to a monolayer GMO along this direction, while those of the \(B_{1u}\) and \(B_{2u}\) modes vary only slightly. Although interactions between the layers of GMO and graphene have little effect on the frequencies of the modes, the \(B_{2u}\) and \(B_{3u}\)(\(B_{1u}\)) modes shift to \(~1,202\) cm\(^{-1}\) and \(~520\) cm\(^{-1}\) (\(~1,051\) cm\(^{-1}\)) for a multilayer GMO when the layer spacing is between 3.75Å to 4.0Å. Finally, the effect that the frequency of the \(B_{2u}\) mode is greatly enhanced due to the interaction between adjacent GMO layers can be used to identify the number of layers for a few-layer GMO.

### 3.2 Tunabe Electronic Properties

Calculations of the electronic properties of GMO were carried out using the Full-potential Linearized Augmented Plane Wave (FLAPW) method as implemented in \(flair\)\(^{187}\). A plane wave cutoff of 275 eV was used for the expansion of the wave functions, the Brillouin zone was sampled using a \(12\times12\times 1\) mesh, and the GGA-PBE\(^{155}\) for exchange-correlation was used. A sphere radius of 1.2\(a_B\) was used for both C and O atoms. The internal atomic positions of all the atoms were fully relaxed (\(3\times10^{-3}\) eV/Å) for each set of parameters.
Fig. 3.6 (a) shows the crystalline structure of GMO. Each C atom forms four bonds, two along the zigzag direction to the neighboring C atoms, and two with the bridging O atoms along the armchair direction. The two-dimensional centered-rectangular (quasi-hexagonal) structure can be described by two of three interrelated parameters: the length of the rhombus edge, $a_o$, the opening angle $\alpha$ (equal to 120° for hexagonal systems), and the width of the conventional rectangular cell ($d_{O-O}$ in Fig. 3.6(a)). For the fully relaxed ground state structure ($a_o=3.10$ Å, $\alpha=130^\circ$), the C-C bond length (1.56 Å) is close to the typical values (~1.54 Å) of sp³ C bonds, while the C-O bond length (1.43 Å) is comparable with sp² C-C bonds (1.42 Å). Since the stiffness of graphene is strongly dependent on the planar sp² σ bonds, the large C-C bond lengths compared with those of graphene suggest (and are borne out by the calculations) that GMO is less rigid than graphene. The higher electronegativity of O (3.44) than that of C (2.55) is consistent with the calculated result [cf., Fig. 3.6 (b)] that electrons accumulate near the C-O bonds and the O atoms.

The calculated trends in the distortion energies of GMO as a function of $\alpha$ and $d_{O-O}$ are shown in Fig. 3.7(a). The energy cost for rather large distortions is small, and the “energy valley” is approximately aligned along constant $a_o$ (=3.10 Å). External strains are accommodated mainly by changes in $\alpha$ (or equivalently, $d_{O-O}$) rather than by changes in $a_o$: The low-energy structure has a modulus of ~570 GPa along the zigzag direction, about half of the graphene modulus (~1.1 TPa). Fig. 3.7 (b) presents the calculated band gaps corresponding with the structure parameters in Fig. 3.7(a). (Although the gaps are likely underestimated, as is common in DFT calculations, the trends and overall band topologies are expected to be valid.) For the fully optimized structure, GMO is a
A semiconductor with a calculated indirect band gap of ~0.6 eV. Upon planar deformation, GMO spans the range of semiconducting (both indirect- and direct-gap GMO(IGMO and DGMO)) and metallic behaviors. Stretching along the zigzag direction (increasing \(d_{O-O}\)), causes the band gap of GMO to vary from ~0.6 eV (indirect-gap, at 130°) up to ~1.4 eV (both indirect- and direct-gap, at 126°), then down to ~0.1 eV (direct-gap, at 121°). The sensitive response of the band gap to external strains in GMO could be attractive for low-cost fabrication of building blocks in nanoelectromechanical systems (NEMS).

Fig.3.6 The structure and difference charge density of GMO. (a) Perspective and top views of GMO in a 3×3 cell with lattice parameters labeled. C (O) atoms are represented by yellow (red) balls; all C atoms are in the same plane. (b) Side views of the difference between the self-consistent and overlapping atomic electron densities (\(\Delta n=n_{C0}-n_{C-n_{O}}\)) of GMO. Light blue and green isosurfaces (±0.05 e/\(a_B^3\)) indicate accumulation and depletion of electrons, respectively.
Fig. 3.7 (a) Distortion energies relative to the fully relaxed GMO structure per CO formula unit as functions of the structural parameters $\alpha$ and $d_{O-O}$ given in Fig. 1(a). The black star represents the lattice parameters of the fully relaxed structure; the blue line indicates a constant $a_0=3.10$ Å. (b) Calculated band gap of GMO as a function of $\alpha$ and $d_{O-O}$. The calculated crossover between the direct and indirect gap is indicated by the dashed line. Calculated bands for $a_0=3.10$ Å in (c) $\alpha=130^\circ$ and (d) $\alpha=125^\circ$. The inset in (c) shows the symmetry lines and points in the Brillouin zone for GMO. Since the point group symmetry of GMO is $D_{2h}$, compared with the $D_{6h}$ symmetry of graphene, the K’ point in GMO has no additional symmetry compared with other points along $\Delta’$. The effective mass labels indicate light and heavy electrons ($m^{*}_{Le}$, $m^{*}_{He}$) and holes ($m^{*}_{Lh}$, $m^{*}_{Hh}$).

In contrast, graphene is not an ideal candidate for NEMS, since the electronic structure of graphene is robust against external strains up to $\sim 23\%$\textsuperscript{190} while the fracture strain is $\sim 25\%$\textsuperscript{191}. Although the band gap of GNR with armchair edges has been theoretically predicted to be tunable by mechanical perturbations and may have a semiconductor-metal transition as the strain increases\textsuperscript{192}, the uniaxial modulus of these GNRs is extremely large, $\sim 7$ TPa\textsuperscript{193}, imposing severe constraints for practical NEMS system applications.

To tailor the semiconducting behavior of the graphene-based materials, it is necessary to understand the origin of the states around the Fermi level. Representative band structures, for the same $a_0$, but different angles $\alpha$, are shown in Figs. 3.7(c) and (d). The low-lying conduction bands exhibit large variations, while the valence bands have small changes, as
α varies from 130° to 125°: The conduction band state labeled Γ_{C1} (X_{C1}) undergoes an upward (downward) shift of ~0.8 eV (2.6 eV), while X_{V1} moves down ~0.1eV. Such band shifts are indicative of significant changes in the interactions between atomic orbitals on different sites with respect to angle α for a fixed lattice constant a_o. Figs. 3.8 (a)-(d) present the charge density distributions corresponding with the states at the top and the bottom of the gap, as labeled in Figs. 3.7(c) and (d). The conduction band edge states (Γ_{C1} and X_{C1}) exhibit different characteristics, with X_{C1} having no O 2p contributions. On the C atoms, the conduction states are predominantly p_z for Γ_{C1} (IGMO), whereas for X_{C1} (DGMO) there is a strong admixture of p_x. The gap edge valence state X_{V1}, on the other hand, is predominantly O p_y (with a small admixture of p_z) and bonding C sp^2 (p_x, p_y) orbitals that would form a conduction network along the zigzag direction for p-doped GMO.

Alternatively, we also can understand the band gap variation through the tight binding method. Tight binding approximation-based analysis was performed within the orthogonal scheme and details can be found in reference^{194}. The position of any atom \( \mathbf{r}_{ij} \) in the \( j^{th} \) primitive cell and the position of the atom \( i \) is given as \( \mathbf{r}_{ij} = \mathbf{R}_j + \mathbf{r}_i \), where \( \mathbf{R}_j \) is the Bravais lattice vector of \( j \)-th unit cell and \( i = 1, 2, 3, 4 \) for GMO. The Hamiltonian \( H \) is the sum of the unperturbed atomic Hamiltonians \( H_0 \) and the interaction term \( H_{\text{int}} \).

Due to the translational invariance, the unperturbed wave function is expressed in the form of Bloch functions \( \Phi_{\mathbf{k}} = \frac{1}{\sqrt{N}} \sum_{m,i} \sum_{j} C_{mi} \exp(i\mathbf{r}_{ij} \cdot \mathbf{k}) \phi_{mi}(\mathbf{r} - \mathbf{r}_{ij}), \)
Fig. 3.8 Charge density isosurfaces (0.05 e/\text{a}_B^3) of states at the top of the valence band (light green) and at the bottom of the conduction band (blue) in top and side views. (a) and (c) IGMO: \Gamma_{C1} and \text{X}_V1 [cf., Fig. 3(a)]; (b) and (d) DGMO: \text{X}_{C1} and \text{X}_V1 [cf., Fig. 3.7(d)].

where $N$ represents the number of primitive cells. By operating on $\Phi \Phi_k$ with the Hamiltonian $H = H_0 + H_{\text{int}}$, the eigenfunctions and eigenvalues can be obtained through a set of linear equations

$$
\sum_{m,i}(H_{m_i, m'_i} - E_k \delta_{m m'} \delta_{ii'})C_{m'_i}(k) = 0,
$$

(3.1)
in which the matrix element

\[ H_{m'i',k'i'}(\vec{k}) = \sum_{i,j}^{N} \sum_{i'j'}^{N} \frac{1}{N} \exp[i(\vec{r}_{ij} - \vec{r}_{i'j'}) \cdot \vec{k}] \times \langle \Phi_{mik} \Phi_{m'i'k'}(\vec{r} - \vec{r}_{ij}) | H | \Phi_{m'i'k'}(\vec{r} - \vec{r}_{ij'}) \rangle. \] (3.2)

Here only the outmost partially occupied orbitals (2s\(^1\)2p\(^3\) for C and 2p\(^3\) for O) are considered and we start with C-C\(_2\)O\(_2\) complex as the block (nearest neighbor for C) in GMO in which the central C1 atom is bonded to 4 pendant atoms (2 C2 atoms and 2 O atoms). When there are no bonds between them, the interactions between C2 and O atoms are also neglected without destroying the validity of the method to extract the most relevant feature in the band structure. The resulting matrix elements are summarized in the Table 3.3.

At \( \Gamma \) point, the parameters \( g_i \) are equal to 0 (2) for even (odd) \( i \). Due to the vanishing value of one of the direction cosines for GMO, the matrix element containing \( V_{y'z'} \) (i,j = null or prime ) turns out to be zero. Now, the 14×14 overlap matrix is reduced into three block matrices, one 6×6 matrix and two 4×4 matrices. It can be seen from the 6×6 matrix that the interactions between the Px orbitals are coupled with S orbitals which are indicative of the \( sp \) hybridization. Thus, it is concluded that bands at \( \Gamma \) point are solely related to the interactions between the C(s,P\(_x\)) \(-O(P_x)\), C(P\(_y\))-O(P\(_y\)), and C(P\(_z\))-O(P\(_z\)). The number of interaction terms have now been greatly reduced to 9, and these terms can be expressed as follows:

\[ V_{ss} = \exp(-d_1/d_{10})V_{ss}\sigma \] (3.3)
where $l_1(2)$ means the directional cosine for C-C (C-O) bond with respect to the x axis, and $d_1(2)(\theta)$ represents the C-C (C-O) bond length at different lattice angles while the subscript $\theta$ indicates the case in fully optimized structure ($a_0=3.10$ Å, $\alpha=130^\circ$). Here the interaction strengths between orbitals are assumed to vary through an empirical exponential factor.

Due to the strong similarity between the local bonding structure of GMO ($sp^3$-like) and diamond ($sp^3$), we used the same approach and adapted values of diamonds for the overlap matrix of GMO, where the values of $V_{ss}$, $V_{sp}$, and $V_{xx}$ are taken as 15.2 eV,
10.25 eV, and 3.0 eV\(^{195}\), respectively. The bands around the Fermi level are related to the interactions between \( p \)

### TABLE 3.3: Matrix elements at general \( k \) point for \( s \) and \( p \) bands in GMO.

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where \( g_{1,2} = \exp(\text{i} \mathbf{k} \cdot \mathbf{d}_1) \pm \exp(\text{i} \mathbf{k} \cdot \mathbf{d}_1') \) and \( g_{3,4} = \exp(\text{i} \mathbf{k} \cdot \mathbf{d}_2) \pm \exp(\text{i} \mathbf{k} \cdot \mathbf{d}_2') \) \( \), prime means electron orbitals from O atom and \( E_s(\mathbf{E}_p, \mathbf{E}_p') \) is energy of \( 2s \) orbital for C atom (\( p \) orbital for C, O atom).
dictated only by the energy of $P_y$ and $P_z$ orbitals. For GMO, the point group is $D_{2h}$ and accordingly, the $P_z$ orbital has a higher energy than the $P_y$ orbital due to the symmetry. Using the same argument, the energy of the $P_x$ orbital lies between the $P_z$ and $P_y$ orbitals. Since the interaction strength is inversely proportional to and relies largely on the bond length (distance), we conclude that the interaction strengths increase from the $p$ orbitals of O-O, to the $p$ orbitals of C-C and to the $p$ orbitals of C-O since the bond length increases gradually for C-O (1.43Å), C-C (1.56Å), and O-O (2.60Å). The corresponding energy level is further away from the Fermi level for both bonding and anti-bonding interactions, while the interactions between $s$ and $p$ orbitals are stronger than those between $p$ orbitals.

Since $\Gamma_{C1}$ and $\Gamma_{C2}$ states determine the gap type of GMO, the softening (strengthening) of specific orbital interactions implies that bands would move down (up). In terms of bond length and reaction strength, the overlap parameter can be expressed as $V_{l'l'm} = \tau_{l'l'm} \hbar^2/m d^2$, where $\tau$ is the geometric factor of the crystal, $l'()$ denotes the interacting orbital, and $d$ is the nearest-neighbor distance. To qualitatively describe the variation of overlap strength between orbitals, the following assumptions are made. First, the geometric factor is an invariant since the crystal symmetry does not change when the lattice angle is varied. Second, note that GMO is a polar material, and $V_{l'l'm}$ depends on $d$ as $d^{2+\alpha}$ with $\alpha > 0(\alpha < 0)$ since more charge will be transferred as the C-C distance increases, with $\alpha = 0$ for the optimized structure. When IGMO is turned all the way into DGMO upon stretch, the pronounced feature is a large increase of the C-C bond length $d_1$ (also for its directional cosine $l_1$), together with a small decrease of the C-O bond
length $d_2$ (also for its directional cosine $l_2$). Reviewing Eqns. (3.6)-(3.11) suggests that $V_{xx}$ and $V_{zz}$ undergo large variations when the lattice angle varies, while $V_{yy}$ experiences a small change and the remaining two terms ($V_{xx'}$ and $V_{yy'}$) fall in between. Since electrons are mostly transferred from the C atom into the $P_z$ and $P_x$ orbitals of the O atom, the $P_x$ ($P_z$) interactions between the C-C (O-O) atoms are expected to weaken (strengthen), while the $P_y$ interaction between O-O atoms is somewhat enhanced. Subsequently, both the bonding (anti-bonding) interaction of the $P_z$ and $P_y$ orbitals between the O-O atoms in the valence (conduction) band will move down (up). Similarly, the bonding (anti-bonding) interactions of $P_x$ orbitals between C-C atoms in the valence (conduction) band will shift up (down). We conclude that the $\Gamma_{v1}$ state is mostly from the $P_y$ orbital interactions between C-O atoms, while the $\Gamma_{c1}$ ($\Gamma_{c2}$) state is mostly from the $P_z$ ($P_x$) orbital interactions between C-C (C-O) atoms.

The band gap (width and type) and the charge carrier mobility – which is inversely proportional to its effective mass – are critical features for semiconductor-based device applications. As shown above, GMO may be either a direct or indirect band gap semiconductor, and it has a tunable band gap. As a measure of the transport properties, Fig. 3.9 shows the effective masses for electrons and holes as a function of the angle $\alpha$. The electron effective masses change dramatically when GMO switches from indirect- to direct-gap semiconductor as a result of the conduction band minimum changing from $\Gamma$ to X. The hole mass along the armchair direction (X to $\Gamma$) remains fairly constant, but there is an increase along the zigzag direction with decreasing $\alpha$. 
Fig. 3.9 Electron (black squares) and hole (red circles) effective masses are shown for anisotropic GMO. The effective masses of carriers with respect to lattice angles are evaluated from quadratic fits to the band dispersion. The transition from IGMO to DGMO is \(~126^\circ\).

In the case of IGMO, the light electrons (preferred conduction) are along the armchair direction, i.e., through the C-O-C double epoxy units; in the case of DGMO, the light electrons are in the zigzag direction through the \(\ldots\)-C-C-C-\(\ldots\) network. For the holes, the preferred conduction is along the armchair direction for both IGMO and DGMO. The calculated GMO effective masses \((m^*_\text{le}/m_e=0.112-0.132, m^*_\text{lh}/m_e=0.185-0.225)\) are larger than those in Ge \((m^*_\text{le}/m_e=0.041, m^*_\text{lh}/m_e=0.044)\) and group III-V semiconductors \((m^*_\text{le}/m_e=0.015-0.11, m^*_\text{lh}/m_e=0.021-0.082)\)\(^{194}\), but they are comparable to those of Si.
(m*_{Le}/m_e=0.20, m*_{Lh}/m_e=0.15)\(^{196}\) and GNR with similar band gaps (m*_{Le}/m_e = m*_{Lh}/m_e =0.075-0.10 for band gaps of 0.2-0.5 eV, with the effective mass drastically increasing above 0.1 when the band gap exceeds 0.5 eV\(^ {197}\)).

GMO as originally observed\(^ {83}\) is likely embedded within a graphene matrix. If GMO is to be incorporated into graphene-based nanoelectronics, understanding the interface between the two materials is essential. To investigate how the interface affects the electronic structure of both graphene and GMO, we consider a simplified model of the combined system, which consists of a periodic array of ~30 Å stripes of both graphene and GMO, with the interface along the zigzag direction and with d_{O-O} of GMO fixed with the corresponding distance in graphene (Fig. 3.10(a)), thus the atoms in the GMO region are relaxed only along the arm-chair direction; at this d_{O-O} GMO is metallic (cf., Fig. 3.7(b)). Although a realistic modeling of the device characteristics of a GMO-graphene hybrid would require far larger cells and the inclusion of disorder, further interface relaxations, and beyond DFT/GGA corrections to the energy bands, the results illustrate the basic effects that will occur at such an interface. Energetically there is a cost related to this distortion of the GMO, but the formation of GMO is still energetically more favorable (by ~ 0.2 eV/O-atom in our calculations) than forming isolated epoxide groups\(^ {198}\) or carbonyl pairs, which are the most stable functional groups in graphene oxide\(^ {199}\).

Fig. 3.10(b) shows the (local) band structure of the combined system in the middle of the graphene region and k-projected (“unfolded”) onto the graphene 1×1 Brillouin zone. In contrast to graphene, there is a band gap of ~0.5 eV at the K’ point – Γ-K’-M corresponding with propagation along the graphene ribbon – with almost linear
dispersion, as shown in the inset. (The bands at the nominally equivalent K’ and K points for pristine graphene are different here.) This induced gap is significantly larger than the gap of ~0.2 eV expected for zigzag GNRs of the same width, pointing out the influence of the graphene-GMO interface. Fig. 3.10(c) shows the local k-projected band structure of the GMO region. The electronic states from graphene extend throughout the ~30 Å wide GMO region: although in pure GMO (cf., Fig. 3.6), there are no states within several eV of the Fermi level at K’, images of the graphene bands shown in Fig. 3.10(b) are clearly seen along Γ-K’-X’ in Fig. 3.10(c). The gap at K’ in the graphene region has increased (doubled) to ~1 eV in the GMO region of the composite. (The bands around K’ display aspects of being at a high symmetry point, which is true for pure graphene, but not GMO, providing further evidence of the leakage of graphene states.) Similarly, there are remnants of the GMO bands in the graphene region, i.e., there is a complicated superimposition and entanglement of graphene and GMO states near the interface. The effects of the lateral confinement and interaction effects due to the finite widths of the ribbons are particularly noticeable along X-Γ (and M-Γ of the graphene) since this is the direction corresponding with propagation across the interface. In the GMO region, there are two sets of bands that form a staircase of states with fairly well-defined momenta and energies. These bands corresponding with those shown in Figs. 3.7(a) and (c); note, that the other bands do not show the same staircase behavior, indicating that the origin of the staircases is not simply confined to the GMO ribbon. These GMO states, in fact, extend into the graphene, and are the dominant states along M-Γ within a few eV of the Fermi level, Fig. 3.10(b).
Fig. 3.10 (a) Interface model of graphene and GMO with $d_{O-O}$ [cf., Fig. 3.6(a)] fixed to the lattice constant of graphene (2.46 Å). The $1\times1$ Brillouin zones with labels for the graphene and GMO regions are indicated. (b) and (c) $k$-projected band structures for graphene and GMO, respectively, in the middle of each region. The inset in (b) is a magnified view of the bands around $K'$ enclosed in the yellow rectangle. (The $k$-projection decomposes the supercell wave functions into momentum components of the $1\times1$ cells, thus “unfolding” the bands; the resulting states are then spatially integrated to give the relative intensities, varying from blue to red, as shown.)

To further explore the tunable electronic properties of GMO by small external mechanical strain, we investigated the effect of uniform compressive strain along the armchair direction of GMO assuming that the hexagonal symmetry of graphene is maintained due to the large difference in Young’s moduli. The Young’s moduli for GMO
and graphene along the zigzag direction are ~0.6 and ~1.1 GPa, respectively. A 2.5% (3.5%) strain changes the angle of GMO from 133.0° to 132.1° (131.7°) at an energy cost of ~60 meV (80 meV); for graphene, the corresponding distortion is 0.5°. In realistic systems, dislocations, rather than uniform expansions/contractions, will form to relieve the strain at the interface. Because of the difference in the bonding of GMO vs. graphene, dislocations are more likely in GMO. Thus, while the graphene at the interface will be strained, the resulting distortions are expected to be much smaller than those in GMO. For a compressive strain of ~-2.5%, GMO is still metallic and the band structure of graphene maintains the same features, except that the graphene band gap decreases to ~0.4 eV. If the strain is increased to -3.5%, however, the band gap of graphene increases to ~0.6 eV and GMO becomes semiconducting; therefore, GMO might also be used as a tool to tune the band gap in graphene at the G-GMO interface. These types of strains could potentially be realized in GMO – piezoelectric/ferroelectric nanostructure devices, allowing the active real-time modification of the band gap.

In summary, first-principles calculations were presented to elucidate the structural, mechanical, and electronic properties of the newly discovered GMO, whose two dimensional crystalline form offers great potential for future electronic applications. The band gap of GMO is found to be sensitive to the lattice angle (120°-134°) and varies between 0 and over 1.3 eV, with the nature of the band gap switching from direct to indirect as the lattice angle increases. The distinctive characteristics of direct- and indirect-gap GMO semiconductors arise from their sensitive electronic response to external mechanical strains. The strong anisotropic nature of DGMO causes electrons and holes to preferentially move along the zigzag and armchair directions, respectively,
minimizing the rate of recombination between electrons and holes, a desirable feature for photovoltaic devices. The band gap opening and quasi-linear band dispersion in the graphene region near the G-GMO interface suggest the G-GMO structures could find potential applications in future semiconductor devices. Finally, the O atoms in GMO could act as adsorption sites for various adsorbates (e.g., gas molecules, metal ions such as lithium ions, and metal-organic complexes), making GMO a potential candidate for applications in sensors and lithium-ion battery electrodes.

3.3 Anisotropic Thermal Conductivity

The thermal properties of GMO were calculated using the plane wave package under the Quantum Espresso distribution\textsuperscript{175}. A norm-conserving pseudopotential was adopted to treat the core electrons with energy (charge density) cutoff up to 80 Ry (800 Ry), while the GGA in the formalism of PBE\textsuperscript{155} was used for the exchange correlation. The Monkhorst-Pack mesh in the Brillouin zone sampling was 13×13×1 and the vacuum region thickness was greater than 15 Å. The force criterion was within 0.001 eV/Å and the structure was completely relaxed prior to the phonon dispersion calculation. For the ground state structure, the lattice parameters of the quasi-hexagonal cell were found to be \(a_0=3.13\text{Å}\) and \(\alpha=130^\circ\). DFPT calculations were then used to compute the phonon frequencies at arbitrary wave vectors in the unit cell. The dynamical matrix was calculated on a 13×13×1 \(q\)-points mesh for a GMO unit cell.

In general, both electron movement and atom displacement in materials contribute to thermal energy transfer; however, for semimetal with a vanishing electron density of state
around the Fermi level (e.g., graphene) and dielectric solids, the electronic contribution is negligible and heat is predominantly carried by the phonon vibrations. The lattice thermal conductivity of crystalline material can be expressed as

$$\kappa_{ph} = \sum_j \int [v_j(q) \cdot \hat{e}]^2 \tau_j(q) C_j(\omega(q)) dq,$$

(3.12)

where $q$ represents the wave vector in the IBZ, $v_j(q)$ is the group velocity of phonon, $\hat{e}$ is a unit vector in the direction of temperature gradient, $\tau_j(q)$ is the life time of phonon, $C_j(\omega)$ is the specific heat capacity, and the index $j$ runs over all the phonon branches. The random nature of the heat conduction process can be reflected in Eqn. (1) by the temperature gradient $\hat{e}$ and phonon mean free path (MFP) $\Lambda = v \tau$. Depending on the sample size $L$, phonon transport can be categorized into two regimes: ballistic ($L << \Lambda$) and diffusive ($L >> \Lambda$) (henceforth, it is only referred to the diffusive case unless stated otherwise). Applicable to other layered structures consisting of aromatic carbon sheets apart from graphite, Klemens et al. have shown that Eqn. (3.12) can be rewritten as

$$\kappa_{ph} = \sum_j \rho_{m,j} \langle v_j \rangle^4 \frac{\omega_{max} \ln \frac{\omega_{max}}{\omega_{min}}}{\omega_{max} T \langle \gamma_j^2 \rangle},$$

(3.13)

where $\rho_m$ is the mass density in the unit cell of crystal, $\omega_{max}$ ($\omega_{min}$) is the upper (lower) limit of phonon frequency in the IBZ, and $\gamma_j$ is the Grüneissen parameter defined as the negative logarithmic derivative of the phonon frequency with respect to volume

$$\gamma_j = -d\ln \omega_j / d\ln V.$$

To avoid the divergence when $\omega_{min}$ approaches zero for two-dimensional crystals, $\omega_{min}$ is limited to the condition that the MFP $\Lambda$ will not exceed the
sample lateral size $L$. For perfect crystals considering only the Umklapp scattering process,

$$
\alpha_{\text{min},j} = \left( \frac{M \langle \gamma_j \rangle^3 \alpha_{\text{max},j}}{2 \langle \gamma_j \rangle^2 k_B T L} \right)^{1/2},
$$

in which $M$ is the mass in the unit cell, $k_B$ is the Boltzmann constant, and $T$ is the temperature. Note that the logarithmic divergence still occurs here for infinite large crystal, and this can be lifted practically by the imperfection scatterings from defects and rough boundaries etc. From the above analysis, all the essential knowledge of phonon dynamics related to the lattice thermal conductivity (e.g., $v_j$, $\gamma_j$, $\omega_{\text{max},j}$) can be obtained from the phonon dispersion in the IBZ.

Fig. 3.11(a) presents the calculated phonon dispersion of monolayer GMO along the high symmetric directions. Since the symmetry of GMO is $D_{2h}$, the high symmetric lines are selected along the $X\Gamma$ (armchair direction in real space) and $\Gamma K$ (zigzag direction in real space) directions, as indicated in the inset of Fig. 3.11(b). As there are four atoms in the unit cell of GMO, there are twelve phonon branches. Of the nine optical phonon branches, three are infrared-active and six are Raman-active in the zone center. Of the three acoustic phonon branches, similar to those in graphene, both the longitudinal acoustic (LA) and in-plane transverse acoustic (TA) phonon branches exhibit linear dispersion away from the zone center, while the out-of-plane transverse acoustic (ZA) phonon dispersion curve displays fewer quadratic features than that of graphene. By taking the derivative of frequency with respect to wave vector $v_j = d\omega_j / dq$, the averaged group velocities along the two high symmetric lines are $\langle v_{\text{LA}} \rangle_{\text{X}} = 1.29 \times 10^4 \text{ m/s}$, $\langle v_{\text{TA}} \rangle_{\text{X}} = 0.69 \times 10^4 \text{ m/s}$.
\( \langle v_{LA} \rangle_{XK} = 0.70 \times 10^4 \text{m/s} \) and \( \langle v_{TA} \rangle_{XT} = 0.77 \times 10^4 \text{m/s} \), respectively. The large difference in the averaged velocity between LA phonon branches arises from the discrepancy in the planar Young’s modulus along the two directions (880 GPa vs. 570 GPa). Likewise, we calculated the velocities and modulus for graphene, and it turns out that \\
\( \langle v_{LA} \rangle_{MT} = 2.18 \times 10^4 \text{m/s} \) with a modulus of 1.3 TPa (XΓ and MΓ are along the same direction).

As a measure of the sensitivity of phonon frequencies to changes in the crystal volume, the Grüneissen parameter \( \gamma \) provides information on the anharmonic interactions between the lattice waves, which reduce the lifetime of individual phonons from infinite to finite. Fig. 3.11(b) shows the resulting Grüneissen parameter \( \gamma(q) \) of the three acoustic phonon branches for monolayer GMO. The ZA mode has a negative \( \gamma \) (~42) around the zone center along the XΓ direction, while it changes into a positive value (12) around the zone center along the ΓK direction. Physically, negative \( \gamma \) implies the phonon frequency increases as the crystal volume (or lattice constant) increases. For the flexural ZA mode, this means the “membrane effect” for graphene also occurs for GMO, but more preferably along the armchair than the zigzag direction. For both LA and TA modes, \( \gamma \)'s are discontinuous across the zone center Γ. When the wave vector is flipped from XΓ to ΓK, the change from negative into positive \( \gamma \) for the LA mode across Γ suggests that atoms in the LA mode will experience a larger interatomic force along the armchair direction as opposed to the case along the zigzag direction if the lateral size of film is expanded. By averaging along the armchair and zigzag directions, we found that the mean values for \( \gamma \)'s are \( \langle \gamma_{LA} \rangle_{XT} = 0.90 \), \( \langle \gamma_{TA} \rangle_{XT} = 0.56 \), \( \langle \gamma_{LA} \rangle_{XK} = 1.97 \) and \( \langle \gamma_{TA} \rangle_{XK} = 1.35 \).
Fig. 3.11 (a) Phonon dispersion for monolayer graphene monoxide, (b) the Grüneissen parameter for the acoustic phonon modes in GMO. The inset in (b) shows the unit cell of centered rectangular GMO in real space and its first Brillouin zone with the high symmetric points and lines labeled.

Out of simplicity for isotropic materials (albeit reasonable treatment), Eqn. (3.13) was derived from the two-dimensional phonon gas model within the relaxation time approximation (RTA), in which the phonon velocity and its lifetime are averaged as

$$\langle v \rangle^2 = \frac{1}{2} \sum_{i=LA,TA} \langle v_i \rangle^2$$

and

$$\langle \tau \rangle^{-1} = \sum_{i=LA,TA} \langle \tau_i \rangle^{-1}$$

over the entire IBZ, respectively. Nevertheless, these assumptions become erroneous for strong anisotropic materials with a high thermal flux along certain directions, and thus the distinct crystalline axis should be
treated separately. Furthermore, to resolve the contribution to the thermal conductivity from the individual phonon mode, Nika and Balandin et al. refined Eqns. (3.13) and (3.14) as

\[ \kappa = \frac{M}{4\pi T h} \sum_{j \neq A} \frac{\omega_{m,j}}{\langle v_j \rangle^2} \int_{\xi}^{\infty} \frac{e^\xi}{(e^\xi - 1)^2} d\xi, \quad \xi = \frac{\hbar \omega}{k_b T} \]

(3.15)

where \( h \) is the layer distance; for GMO, \( h \) is taken as 3.75 Å. Within the framework of Klemens’s theory, the contribution of ZA phonons to the thermal conductivity is treated negligibly due to the quadratic dispersion and colossal Grüneisen parameter. Using Eqn. (3.15), we first investigated the overall performance of GMO in heat conduction. Fig. 3.12 (a) and (b) show the thermal conductivities of GMO along the XΓ and ΓK directions, respectively. In stark contrast, the former is around five times larger than the latter, demonstrating the strong anisotropy of GMO, and heat is predominantly carried along the …-C-O-C-… than the …-C-C-…chains. We also can see that thermal conductivities along both directions exhibit strong size dependence and will saturate at an extremely large size. As the temperature increases, however, the thermal conductivity displays a decreasing feature.

Principally, for anharmonic lattice interactions at a high temperature, the total number of excited phonons with which a given phonon could interact is proportional to \( T \). Considering that the collision frequency is proportional to the number of phonons, \( \Lambda \) is proportional to \( T^{-1} \) as is also true for \( \kappa \). At room temperature with a lateral size ~5 μm, the thermal conductivity along the XΓ direction is calculated as ~3,000 Wm\(^{-1}\)K\(^{-1}\) and comparable with those of other C allotropes with high thermal conductivity. Even
along the ΓK direction, the calculated room temperature thermal conductivity of GMO (≈600 Wm⁻¹K⁻¹) is much larger than the theoretically predicted value of bulk Si (≈150 Wm⁻¹K⁻¹)²⁹.
Fig. 3.12 Color maps of the intrinsic thermal conductivities of GMO as a function of both temperature and lateral size along the XΓ direction in (a) and ΓK direction in (b). (c) and (d) show the thermal conductivity of GMO in (a) and (b) normalized with respect to graphene along the MΓ direction, respectively. The lateral size starts from 2.5 µm so that the calculated thermal conductivity is diffusive, since the mean free paths for GMO are calculated as ~0.48 µm and ~0.13 µm along the armchair and zigzag directions.
As the predicted absolute value has discrepancy due to the use of various methods, it is more reasonable to normalize the thermal conductivity of GMO to a reference material with experimentally measured results. Here, we selected graphene to minimize the overestimation/underestimation by applying the same procedure to predict its thermal conductivity. Since graphene is isotropic, it has been shown that the thermal conductivities along the MΓ and ΓK directions are similar; hence, the normalized thermal conductivities of GMO along the XΓ and ΓK directions to graphene along the MΓ direction can be used to measure how well GMO performs in heat dissipation. Fig. 3.12 (c) reveals that GMO has a thermal conductivity ~80% that of graphene beyond the size of ~5 µm along the XΓ direction. It also suggests that the thermal conductivity of GMO as a functional of temperature has less slope than that of graphene (or GMO has stronger temperature-dependence) due to the greater number of excited phonons. Along the ΓK directions shown in Fig. 3.12(d), however, the thermal conductivity of GMO is around 15% of that of graphene, and this percentage further decreases as the lateral size increases.

In practical applications, interaction with the substrate is inevitable, and how this interaction will modulate the heat transport is significant in designing the surface morphology of substrate; therefore, it offers insights by resolving the individual contribution from the LA and TA phonon modes to the thermal conductivity. Fig. 3.13 (a) shows the normalized thermal conductivity from the LA mode to the TA mode along the XΓ direction. Above room temperature and beyond a large lateral size ~5 µm, heat is largely (~70%) carried by LA phonons. Along the ΓK direction under the same condition, however, Fig. 3.13(b) indicates that TA phonons are dominant in heat propagation.
For graphene, as seen from Fig. 3.13(c), heat is carried slightly more by LA (TA) phonons at high (low) temperature; around room temperature, the two phonon modes contribute nearly equivalently. As such, the interaction of both graphene and GMO with the isotropic substrate would drastically jeopardize the heat dissipation along all directions. For interactions with anisotropic substrates or uniaxial surface rubbings, however, the thermal energy transfer would degrade by at least 50% for graphene, but only ~30% for GMO. Specifically, the LA (TA) phonon vibrates along the armchair (zigzag) direction for heat conduction along the XΓ direction, and thus heat dissipation from the TA (LA) modes would be greatly mitigated for GMO on substrates with surface rubbings along the armchair (zigzag) direction. Alternatively, as the LA (TA) phonon vibrates along the zigzag (armchair) direction for heat conduction along the ΓK direction, heat transport along this direction from TA (LA) phonons would be severely degraded for the surface rubbings along the armchair (zigzag) direction. Accordingly, GMO would
Fig. 3.13 Color maps of the ratio of thermal conductivity from LA mode to TA mode as a function of temperature and lateral size for GMO along the XΓ direction in (a), GMO along the ΓK direction in (b) and graphene along the MΓ direction (c), respectively.
even slightly outperform graphene in heat dissipation when both are placed on a substrate where the surface was rubbed along the armchair direction.

Despite its relatively slow phonon velocities compared with those of graphene, GMO has superior thermal conductivity at large sizes, mostly because the Grüneissen parameters for GMO along the X\Gamma direction are smaller than those of graphene: 0.90 vs. 1.59 for the LA phonon mode and 0.56 vs. 0.59 for the TA phonon mode. Physically, this means the Umklapp limited lattice wave interactions in GMO experience lower anharmonicity. As \Lambda is inversely related to the Grüneissen parameter, thermal conductivity is strongly dependent on it. For instance, by increasing the Grüneissen parameters for GMO along the X\Gamma direction to those of graphene, the thermal conductivity of GMO decreases to about half of that of graphene.

Note that in Eqn. (3.15), both normal and Umklapp processes are considered. Although the normal scattering process does not directly contribute to the thermal resistance, it affects the thermal conductivity by redistributing the phonon modes that could participate in the Umklapp scattering process. Bonini et al\textsuperscript{207} argued that the lifetimes of LA and TA phonons in free-standing graphene show finite values in the long wavelength limit by decaying exclusively into two low-energy ZA phonons and through the normal scattering process for samples larger than ~1 \mu m, since the mean free path for graphene is ~ 0.78 \mu m\textsuperscript{208}. This anomaly can be lifted by isotropic mechanical strain up to 1% when the ZA mode exhibits linear dispersion around the zone center. Nika et al\textsuperscript{203} also showed that TA phonon mode decays into ZA phonons at several wave vectors through the three phonon Umklapp scattering processes. We found that the ZA phonon mode in GMO
shows the linear dispersion around the zone center for both strained (up to 2.0%) and unstrained systems compared with those of graphene, as shown.
Fig. 3.14 Phonon dispersions of the ZA mode around the zone center under isotropic strains for (a) GMO and (b) graphene, respectively. (c) Grüneissen parameters of the LA and TA modes of GMO along the X\(\Gamma\) (upper panel) and \(\Gamma K\) (lower panel) directions with respect to lattice angle. (d) Thermal conductivity of GMO as a function of lattice angle at room temperature and lateral size of 5 \(\mu\)m along the \(X\Gamma\) and \(\Gamma K\) directions. Purple curves in (c) and (d) are fittings.

in Fig. 3.14(a) and (b). Hence, this linear dispersion may give rise to relatively smaller Grüneissen parameters for the LA and TA phonon modes in GMO along the \(X\Gamma\) and \(\Gamma K\) directions.

Analogous to graphene\(^{209}\), strain also could be used as an approach to tune the heat transfer in GMO in addition to interactions with substrate. Eqn. (4) states that the thermal conductivity from each mode is related to its phonon velocity, Debye frequency, and Grüneissen parameter. Here, we found that phonon velocity and Debye frequency change only slightly with respect to strain. Fig. 3.14(c) shows that the Grüneissen parameter for the LA mode in GMO along the \(X\Gamma\) direction undergoes small variations with respect to the lattice angle, while those of the LA mode along the \(\Gamma K\) direction and TA mode along both \(X\Gamma\) and \(\Gamma K\) directions increase notably (decrease slightly) as the lattice angle decreases (increases). For graphene, it has been shown that the thermal conductivity is very sensitive to the Grüneissen parameters\(^{205}\). For GMO with strain up to \(~10\%\) (126°)
along the zigzag direction when it turns into a direct bandgap semiconductor, Fig. 3.14(d) shows that the thermal conductivities along both \( X\Gamma \) and \( \Gamma K \) directions decrease all the way down to \(~55\%\) of the unstrained systems; however, for tensile strain along the armchair direction, the thermal conductivities increase along the \( X\Gamma \) and \( \Gamma K \) directions, resulting from the decreased Grüneissen parameters. Unlike the unstrained GMO, the linear dispersion around the zone center is disrupted for the strained system; thus, the decreased Grüneissen parameters could be due to the shrunken phase space for the occurrence of Umklapp scattering.

In summary, we have shown that the room temperature intrinsic lattice thermal conductivity of monolayer GMO (\( >\sim 3,000 \text{ Wm}^{-1}\text{K}^{-1} \)) along the armchair direction is indeed superior, and is \(~80\%\) of that of graphene for large lateral sizes \( (>\sim 5\mu m) \) via first-principles calculations within the framework of Klemens’s theory. The predicted thermal conductivity will be around the upper-bound of future experimental measurements due to imperfections in samples. Unlike the isotropic graphene, heat in GMO largely propagates along the armchair direction and the thermal conductivity is about five times larger than that along the zigzag direction. This anisotropy offers opportunities for engineering the heat dissipation in GMO by modifying the surface morphology of substrates. Note that for low temperatures and small lateral sizes (ballistic regime) when the current approach fails, GMO is anticipated to have an even higher thermal conductivity. The high thermal conductivity of semiconducting GMO renders it as an appealing candidate for future logic digital circuit applications.
3.5 Summary

In this chapter, we have calculated the vibrational, electronic and thermal properties of GMO. Monolayer GMO has three infrared active modes: the $B_{1u}$, $B_{2u}$ modes and $B_{3u}$ mode with frequencies of $\sim$1,025 cm$^{-1}$, $\sim$1,096 cm$^{-1}$ and $\sim$523 cm$^{-1}$, distinctive from the four primary bands around 1,560 cm$^{-1}$, 1,350 cm$^{-1}$, 1,250 cm$^{-1}$ and 1,050 cm$^{-1}$ in GO. For multilayer GMO, the interaction between adjacent layers enhances the frequency of the $B_{2u}$ mode, which can be used to identify the number of layers for GMO with few layers. Electronically, GMO is semiconducting and its band gap is sensitive to the external strain, varying between 0 and over 1.3 eV with the nature of the band gap switching from direct to indirect as the lattice angle increases. The strong anisotropic nature of GMO causes electrons and holes to preferentially move along the zigzag and armchair directions, respectively. In addition, GMO possesses superior thermal conductivity and it has been shown that the room temperature intrinsic lattice thermal conductivity of monolayer GMO ($\sim$3,000 Wm$^{-1}$K$^{-1}$) along the armchair direction is $\sim$80% of that of graphene for large lateral sizes ($\sim$5 μm). However, unlike isotropic graphene, heat in GMO largely propagates along the armchair direction and the thermal conductivity is about five times larger than that along the zigzag direction. The carrier mobility (i.e., electronic conductivity) anisotropy suppresses the rate of recombination between electrons and holes in photovoltaic devices, while the heat conductivity anisotropy offers opportunities for engineering the heat dissipation in GMO by modifying the surface morphology of substrates. The suitable band gap, and the high electronic and thermal conductivities of GMO render it an appealing candidate for future logic digital circuit applications.
CHAPTER 4 ENGINEERING MAGNETIC PROPERTIES OF ZGNR THROUGH EPOXY CHAINS

Unlike electronic devices, spintronic devices invoke both the charge and the spin degree of freedom of carriers, and thus are promising in quantum information processing, storage, and communication via the transport of spin-polarized current\textsuperscript{210}. Among the carbon allotropes, graphene has sparked intense interest due to its Dirac fermion behavior that leads to unprecedented high carrier mobility, even at room temperature ($\sim 10^6$ cm$^2$/Vs)\textsuperscript{8}. Hence, graphene offers great potential for future spintronic applications if the magnetism can be produced\textsuperscript{211-213}. In this chapter, we study the magnetic properties of zigzag graphene nanoribbon (ZGNR) oxidized by either single epoxy or epoxy pair chains using the first-principles calculations.

4.1 Geometric Structures and Magnetic Properties of Oxidized ZGNR

Magnetic materials that are widely used today are composed of elements from the $d$- or $f$-block of the periodic table that possess the partially filled $d$- or $f$-bands and thus give rise to magnetism\textsuperscript{214}. It is not common for the light $p$-block elements to show magnetism, regardless of the partially occupied $p$-bands\textsuperscript{211}. However, it would be beneficial to generate magnetism in the light elements or carbon-based materials, as their trivial spin-orbit coupling prevents the decoherence of the aligned spins, and thus long magnetic
order could be potentially realized, even at a relatively higher temperature\textsuperscript{215}. For example, the spin relaxation time is anticipated to be greater than 0.1 μs in these light elements, since this length of time has been supported in light metals\textsuperscript{216}. To this end, the diverse structures of carbon-based materials have attracted significant attention.

The honeycomb lattice of graphene involves the $sp^2$ hybridization and the $\pi$ ($\pi^*$) bands are formed from the $p_z$ orbitals of the neighboring C atoms, which govern its electronic properties. Pure and infinitely large graphene is nonmagnetic due to the fully occupied $\pi$ bands. Within the framework of Hubbard model\textsuperscript{217}, this can be understood based on the bipartite lattice, where the sublattices A and B in graphene are filled with an equal number ($N_A = N_B$) and the total spin moment $S=|N_A-N_B|/2$ is thus zero. Consequently, the introduction of magnetism necessitates the breaking of the paired $p_z$ orbitals, which gives rise to the occupation imbalance between the A and B sites. This can be accomplished by creating vacancies/defects\textsuperscript{218} in pristine graphene and the H passivation\textsuperscript{219} of certain sublattice or N doping\textsuperscript{220}, which would leave effective dangling bonds of the first nearest neighbors of the vanished, passivated, and substituted sublattices, and the spin density would decay away from these neighbors due to the proximity effect. These dilute moments could also be induced by depositing magnetic elements on the graphene surface, depending on both the local environment and the element species\textsuperscript{221}.

Another promising route is to cut graphene into zigzag nanoribbons, since the occupation number difference of the sublattices A and B is two compared with zero for armchair nanoribbons\textsuperscript{222} and graphene. Moreover, the theoretically predicted spin wave stiffness constant (2,100 meVÅ\textsuperscript{2}) for ZGNR\textsuperscript{215} is much higher than that for $d$ element-based magnetic materials like iron\textsuperscript{223}, suggesting a higher Curie temperature in carbon-based
materials\textsuperscript{224} and potential operation near room temperature. This can also be seen from the spin correlation length of \(~1\) nm at 300 K\textsuperscript{215}. The ground state of ZGNR shows antiferromagnetism with a small energy band gap and vanishing total spin moment, which is not beneficial for spintronic applications. Consequently, transition from the antiferromagnetic (AFM) to ferromagnetic (FM) semiconductor for ZGNR is desirable, and approaches to realize this include inserting into it a line defect of pentagon-pentagon-octagon\textsuperscript{225} and applying external uniaxial strain\textsuperscript{226,227}.

Although the magnetic moment has been experimentally observed in RGO\textsuperscript{228}, which includes vacancies, defects, and residual functional groups like epoxide, it is still unknown whether the epoxide group and its arrangement can induce local moment. This is significant, because electronic properties of graphene exhibit rich variety via oxidation manipulation\textsuperscript{177}. Here, we investigate the magnetic properties of ZGNR oxidized by single-epoxy/epoxy-pair chains from the DFT calculations. The reasons to consider the epoxy pair are three-fold: (1) The epoxide group favors aggregation and lining up energetically on one side of graphene upon oxidation\textsuperscript{66,229}, but the epoxy pair structure is favored\textsuperscript{198,230} when both sides of graphene are oxidized and it is thermodynamically stable, even up to a high temperature (1,000 K)\textsuperscript{231}. Moreover, the formation of the energy barrier of the epoxy pair chain decreases as its length increases\textsuperscript{232}, and the formation can be further facilitated by applying external uniaxial strain, especially along the zigzag direction\textsuperscript{233}. (2) Such domains of epoxy pair structure have been experimentally identified\textsuperscript{83} and are predicted to be semiconducting\textsuperscript{234} with superior heat dissipation power\textsuperscript{235}. Its synthesis can also be inspected by examining the characteristic bands from the infrared spectrum\textsuperscript{236}. (3) The heterostructure between the epoxy pair and graphene
opens a finite band gap in the graphene region with quasilinear dispersion, and it is intriguing to explore further its impact on the magnetic properties.

The DFT calculations were carried out by the code OPENMX. The pseudo atomic orbitals (PAOs) were used to represent the basis functions and were specified by H6.0-\(s^2p^2\), C6.0-\(s^2p^2d^1\) and O6.0-\(s^2p^2d^1\), where 6.0 is the cutoff atomic radius in Bohr, and \(s^2p^2d^1\) indicates that basis functions are expanded by two primitive orbitals for individual s and p orbitals and one for d orbital. The exchange-correlation functional was the spin-polarized GGA-PBE. In order to accurately obtain the small energy difference between the AFM and FM systems, the numerical integrations were performed with large cutoff energy of 400Ry in real space and the k-point separation of 0.02/Å along the reciprocal lattice vectors. The structural relaxations were terminated when the force between the successive iterations was within 0.001 eV/Å.

We began investigating the electronic and magnetic properties of ZGNR oxidized by epoxy chains using the 8ZGNR as the prototype. Fig. 4.1a shows the unit cell of 8ZGNR with the atomic species and identity number of each individual atom specified. The position of epoxy chain shifts from the edge into the interior. The epoxy pair sits both above and below the C plane with the underlying C bond broken, and only one chain is considered, as shown in Fig. 4.1b. For the regular epoxy bridging the underlying two C atoms in Fig. 4.1c, the unit cell of its ground state structure is doubled compared with that of epoxy-pair-chain-oxidized 8ZGNR, but the oxygen to carbon ratio is kept the same for the two structures. Here, we label the two structural scenarios as 8ZGNR-ep_n and
8ZGNR-e_n, where ep and e represent the epoxy pair and epoxy chain, respectively, and n represents the position of these chains. Fig. 4.1 d presents the energy difference per oxygen atom in the systems of nonmagnetic ground state relative to 8ZGNR-e_1, which is the most energetically favored structure among the systems we considered. It can be

Fig. 4.1 (a) Top view of the unit cell of 8ZGNR with each atom labeled with the atomic species and the position number. (b) and (c) are the top and side views of the unit cell of 8ZGNR-ep_1 and 8ZGNR-e_1, respectively, where the position is defined in (a). (d) Energy difference per oxygen atom in the systems of nonmagnetic ground state relative to 8ZGNR-e_1.

observed that the epoxy pair chain prefers sitting in the center of the ribbon as opposed to the single epoxy chain, which is bonded at the edge. However, when the number of
carbon chains increases from 8 to 16, the energy difference between the two structural scenarios (i.e., 16ZGNR-e_1 vs. 16ZGNR-ep_8) decreases from 0.41eV/O to 0.32eV/O.

Next, we consider the effect of epoxy pair and epoxy chains on the magnetic properties of 8ZGNR. Fig. 4.2a shows the spin moment projected to each individual atom in the 8ZGNR-ep_n structures when the coupling across the edges is FM. For pure 8ZGNR, the total moment in the unit cell is 0.57 \( \mu_B \) and the spin moment for the edge C atom is 0.30\( \mu_B \), which is similar to the reported values in ZGNR \textsuperscript{215,222,225}. For 8ZGNR-ep_1, the total moment increases to 1.15\( \mu_B \), which is twice that of 8ZGNR. This is primarily due to the moment enhancement of atoms C1(0.48\( \mu_B \)), C4(0.24\( \mu_B \)), and C6(0.12\( \mu_B \)), and the moment generation of 0.16\( \mu_B \) in total by oxygen atoms. Note that atoms C1 and C4 are the first nearest neighbors for C2 and C3, respectively, which are bonded to the epoxy pair; therefore, the increased moment is intimately correlated with the epoxy pair.

Mulliken charge analysis reveals that the total charge (charge projected into the \( p_z \) orbital) is 3.949e (0.957e), 3.941e (0.979e), 3.999e (0.984e), and 3.997e (0.978e) for atoms C1, C2, C3, and C4 in 8ZGNR, respectively, while it is 3.866e (0.968e), 3.676e (0.664e), 3.659e (0.618e), and 3.933e (1.006e) for atoms C1, C2, C3, and C4 in 8ZGNR-ep_1, respectively. This suggests the \( \pi \) bonding between atoms C1-C2 and C3 - C4 is impeded by the oxygen atoms bonded to C2 and C3, thereby decreasing the total charge, but increasing the charge in the \( p_z \) orbital for atoms C1 and C4, which might be responsible for the moment enhancement. This underlying mechanism is similar to that of the atomic-hydrogen-adsorbed graphene sheet, which shows magnetism due to the unsaturated neighbors of the \( sp^3 \) carbon bonded with hydrogen\textsuperscript{219}. In fact, such electron transfer can also occur among \( \pi \) orbitals for the edge-located atoms or border atoms in the
heterojunctions between carbon and other first-row elements due to different electron negativities\textsuperscript{237}. Despite that both \( s \) and \( p_{x,y,z} \) orbitals contribute to the spin moment, the large contribution primarily comes from the \( p_z \) orbital.

The spin-polarized charge density in Fig. 4.2a also indicates the epoxy pair chain will separate the ZGNR (regardless of its width) into the zigzag-shaped subregions and demonstrate similar spin-density distribution as in ZGNR. The trend analyzed for 8ZGNR-ep_1 also holds as the epoxy pair chain moves from the edge into the interior, except that the total moment in the unit cell increases to \(~1.38 \mu_B\). The increased moment is related to one of its two nearest neighbors of epoxy pair, which coincide with the edge atom C1 for 8ZGNR-ep_1. For the AFM coupling, the spin moment distribution of 8ZGNR presents the spatial inversion symmetry with respect to the center of the ribbon and the total moment is thus zero. For 8ZGNR-ep_n structures, however, the total spin moment is finite (0.57 \( \mu_B \)), as shown in Fig.4.2b, except that the 8ZGNR-ep_1 structure keeps this inversion symmetry and thus shows the trivial total moment. The underlying rationale for the spin moment enhancement is the same as that for the FM coupling; in fact, comparison between the moment distribution in FM and AFM couplings in Fig.4.2a and b suggests that only the subregion with reversed spin of the edge atom (i.e., AFM coupling) exhibits the moment rearrangement, while the moment distribution in the other subregion remains intact.
Fig. 4.2 Atomic site-resolved spin moment distribution of oxidized 8ZGNR. (a) and (c) are the FM and (b) and (d) are the AFM coupling for 8ZGNR-ep_n and 8ZGNR-e_n, respectively. The empty circles with drop lines are the atomic spin moment for pure 8ZGNR compared with its oxidized counterparts. The cyan (light yellow) areas indicate the carbon atoms bonded to oxygen atoms and their first nearest neighbors (the oxygen...
atoms). The right panel of each figure is the spin-polarized charge density isosurface $(|4.65 \times 10^{-2} \, \text{e/Å}^3|)$ for 8ZGNR and 8ZGNR-ep_1/8ZGNR-e_1. Red and green colors represent the spin-up and spin-down electron densities, respectively. Considering that the carbon atom in the unit cell has the same moment as its counterpart when the cell is divided into two unit cells of 8ZGNR, the moment distribution is thus shown for only a half unit cell in (c) and (d).

To illustrate the roles of single epoxy, Fig. 4.2 c shows the spin moment distribution for 8ZGNR-e_n structures for the FM coupling. Total moment in the reduced cell is lowered to 0.43 $\mu_B$ with respect to 0.57 $\mu_B$ for 8ZGNR; this degradation is due to both the edge carbon atoms near the epoxies and the nearest neighbors of carbon atoms in epoxies. Specifically, the moment for the edge atom C1 is almost zero for 8ZGNR-e_1 and is reduced from 0.30 $\mu_B$ to 0.14 $\mu_B$ for 8ZGNR-e_2(3). The two nearest carbon atoms of epoxy exhibit opposite signs of moment (e.g., atoms C2 and C7 in 8ZGNR-e_2, which have the moment of -0.11 $\mu_B$ and 0.20 $\mu_B$, respectively), contrary to those of epoxy pairs. Moreover, the contribution to the overall moment from oxygen atoms is negligible. When the coupling across edges is switched into AFM, the total spin moment becomes trivial, as shown in Fig. 4.2 d, just like that of ZGNR. Therefore, it can be concluded that the epoxy chain in ZGNR is not beneficial for enhancing magnetism.
Fig. 4.3 Upper panel: The energy difference per edge carbon atoms of 8ZGNR, 8ZGNR-ep_n, and 8ZGNR-e_n with both AFM (black-filled square) and FM (red filled circle) couplings with respect to the spin-unpolarized ground state. Lower panel: The exchange coupling strength for the nearby edge carbon (C1) atoms.

For spintronic applications, it is necessary to consider the energy difference between the spin-polarized and unpolarized states in order to estimate the temperature range with which the spintronic devices operate. In the upper panel of Fig. 4.3, the total energy difference per edge carbon atom is shown for 8ZGNR, 8ZGNR-ep_n, and 8ZGNR-e_n structures. The ground state of 8ZGNR is predicted to be AFM, and its energy difference with respect to the spin-unpolarized state is 45 meV. Moreover, the tiny energy difference of 1 meV between the AFM and FM states suggests that extremely low temperature is a prerequisite for ZGNR to operate in the AFM state, or the transition from
the AFM to FM states can be easily stimulated by thermal vibrations. By inserting the epoxy pair chain, the 8ZGNR-ep_n structures exhibit either a comparable or greater (e.g., 8ZGNR-ep_2) energy difference, suggesting they are more likely to operate at a higher temperature. For the epoxy-chain-oxidized 8ZGNR, however, the energy difference decreased to below 30 meV, indicating that a temperature lower than that for pure 8ZGNR is required for 8ZGNR-e_n structures to work in the spin-polarized state for spintronic applications. For both 8ZGNR-ep_n and 8ZGNR-e_n structures, the energy differences between the AFM and FM states vary from 0 meV (for 8ZGNR-e_3) to 5 meV (for 8ZGNR-ep_4), and thus the transition between the two states can be obtained via moderate thermal perturbation, just as in 8ZGNR. Note that the ground state is AFM for 8ZGNR and 8ZGNR-e_n structures, but it alternates between AFM and FM for 8ZGNR-ep_n structures as the position of the epoxy pair chain shifts. We also investigated the exchange coupling strength J within the Heisenberg model for the edge (C1) atoms. As shown in the lower panel of Fig. 4.3, the introduction of either epoxy pair or single-epoxy chains into 8ZGNR weakens J, indicating the shortening of the coherence length for the edge-aligned spins—this effect is not beneficial for spintronic applications, and it is more pronounced for the 8ZGNR-e_n systems. Further inspection shows that J decreases as the epoxy-pair or single-epoxy chain moves inwards.
4.2 Electronic Band Structures of Oxidized ZGNR

(a) 8ZGNR

(b) 8ZGNR-ep_1
Fig. 4.4 Band structures for (a) 8ZGNR, (b) 8ZGNR-ep_1, (c) 8ZGNR-ep_4, and (d) 8ZGNR-e_1, respectively. For the spin-polarized band structures, both the AFM and FM couplings are considered and the dashed lines represent electronic states upon the application of the external transverse electric field along the ribbon-width direction. The red and blue lines represent the spin-up and spin-down states, respectively.
To manifest the variations of the electronic structures due to the introduced epoxy pair and epoxy chain, we started with the band dispersions for pure 8ZGNR, as shown in Fig. 4.4a. Without considering spin, 8ZGNR is a half-metal, and a flat band appears at the Fermi level that extends from about one-third of the edge towards the zone center. This flat band arises from the unsaturated π states of edge carbon atoms (mostly from C1 and C16 atoms) and is responsible for the magnetism. In principle, these edge (border) states also exist in the edges of other nonmagnetic light elements, such as B, N, or their heterojunctions\textsuperscript{237}, with carbon sheets that give rise to the so-called flat band antiferromagnetism/ferromagnetism. The edge states around the Fermi level can be reduced/removed by introducing vacancies along the edge or impurities, and thus cause spin suppression\textsuperscript{238}.

A direct band gap (~0.4 eV) can be opened when the AFM coupling occurs for the spin-polarized states across the edges. In this case, the spin-up and spin-down states are predominantly located at one of the edges. Upon the application of the finite external transverse electric field along the ribbon-width direction (e.g., $\varepsilon=0.2$ eV/Å), the band gap for the spin-up states widens while it narrows for the spin-down states, consistent with the calculations by Y. Son et al\textsuperscript{222}. This suggests that the gap for the spin-down states can be closed with a sufficiently large electric field, and the graphene ribbon can be transformed into a half metal\textsuperscript{222}. When the coupling between the ribbon edges is turned into FM, the graphene ribbon is metallic-like for both spins. Unlike the AFM coupling, the applied transverse electric field opens up the band gap for both spin-up and spin-down states, but the overall properties remain metallic-like. In fact, the ribbon can be
transformed into either a half-metal, if it is gate-biased, or a semiconductor, if the electric field is large enough.

When 8ZGNR is oxidized by the epoxy pair chain, the electronic structures will be essentially modified. In Fig. 4.4b, the spinless band structure for 8ZGNR-ep_1 shows that it is metallic-like, despite an indirect band gap (0.6 eV) between the bands in the range of 0.7~1.4 eV, and it will be semiconducting only when its Fermi level is tuned within the gap by a gate voltage or surface chemical doping. For the AFM coupling, there are hole pockets for the spin-up states and an indirect band gap (1.0 eV) between the valence and conduction bands. The spin-down states are metallic-like, suggesting that 8ZGNR-ep_1 can become half-metallic by adjusting its Fermi level, thereby offering potential applications\textsuperscript{239}.

For the FM coupling, we can see from Fig. 4.4b that its electronic structures are quite similar to those of the AFM coupling, indicating that the electronic and magnetic properties of 8ZGNR-ep_1 are governed largely by the temperature rather than the spin-coupling across the ribbon edges. As the epoxy pair chain moves from the edge into the interior, the electronic structure undergoes variations only around the Fermi level, which is also true for wider ribbons\textsuperscript{240}. For example, in Fig. 4.4c, the band structures for 8ZGNR-ep_4 show that the band gap increases to 1.6 eV when the spin is not considered. For the spin-polarized band structure with both AFM and FM couplings, the spin-down energy state at the top of the valence band around X moves down and the band gap is open for the spin-down state; therefore, 8ZGNR-ep_4 becomes semiconducting for both spin and spinless systems when it is moderately gate-biased. Moreover, these properties are less dependent on the external transverse electric field.
For the 8ZGNR oxidized by the epoxy chain, Fig. 4.4d shows that electronic properties of 8ZGNR-e_1 are similar to those of pure 8ZGNR for several reasons: (1) both are half-metal without spin consideration; (2) they are semiconducting (metallic-like) when it is AFM (FM) coupling; and (3) the spin-polarized band dispersions (especially near the Fermi level) can be modified by the transverse electric field because the spin moment is localized largely at the edge atoms. Furthermore, unlike the epoxy pair chain in 8ZGNR, the position of the epoxy chain is found to have a small impact on its band structures; thus, it can be concluded that epoxy chain in GNR plays a small role in manipulating its electronic properties.

4.3 Electronic Band Structures of Oxidized Graphene

Although the ZGNR itself can be tuned from FM metal to half-metal and to semiconductor, it requires a sufficiently large transverse electric field, especially for transition into the semiconducting state. It was reported that these transitions can occur without the external electrical field in the presence of topological line defects of octagons and pentagons by applying the uniaxial strain along ribbon axis direction\(^{226,227}\). However, an extremely large strain (>16%)\(^{226}\) is necessary for the FM semiconductor to happen, which makes the stretching undesirable due to the large Young’s modulus of graphene (~1.0 TPa)\(^{189}\).

As previously discussed, Fig. 1d shows that the regular epoxy-chain-oxidized 8ZGNR structures (8ZGNR-e_n) are energetically favored over the epoxy-pair-oxidized counterparts (8ZGNR-ep_n), and it can be argued whether the epoxy-pair-oxidized nanoribbons can actually exist. For this purpose, we consider the scenarios that graphene
is oxidized by both regular epoxy and epoxy pair chains along the zigzag direction with
the same number of C chains (8) in the unit cell, as shown in the upper panels in Fig. 5. It
turns out that epoxy pair is energetically favored in such a case by 0.23eV/O, and thus
suggests the following strategy to fabricate the epoxy-pair-oxidized-ZGNR: First, the
epoxy pair chains can be produced by oxidizing the graphene on both sides in the oxygen
plasma environment\textsuperscript{229}, and the strains along the armchair direction can be applied to
facilitate the formation of the epoxy pair chains\textsuperscript{177}. Second, such oxidized graphene can
then be cut into nanoribbons, manipulating the width using nanoparticle etching
techniques\textsuperscript{241}. Lastly, the edges of ribbons should be passivated by H atoms.

For comparison with the oxidized nanoribbons, electronic structures of the oxidized
graphene are presented in the lower panels of Fig. 4.5. The regular epoxy-chain-oxidized
graphene is an indirect band gap semiconductor with the energy gap of 0.12 eV, which
increases to 0.35 eV when spin is considered for both the AFM and FM couplings.
Moreover, the AFM and FM electronic structures in Fig. 4.5a are almost identical,
suggesting that the different spin couplings have little effect on its electronic structures.
For the epoxy-pair-oxidized graphene, both the spinless and spinful systems are metallic-
like due to the states from the epoxy pair chain; however, the energy gap present in the
epoxy-pair-oxidized nanoribbons disappears and thus it is impossible to tune the epoxy-
pair-oxidized nanoribbon into a semiconductor or half-metal. For the AFM coupling,
both the regular epoxy- and epoxy-pair-oxidized graphene have trivial spin moment,
even for individual atoms, i.e., the AFM coupling is equivalent to the nonmagnetic state;
whereas for the FM coupling, the spin moment in the epoxy-oxidized graphene is 0.41μ\textsubscript{B}
in the reduced cell, larger than the 0.26 μB in the unit cell of epoxy-pair-oxidized graphene. Although the ground state for the epoxy-oxidized
Fig. 4.5 Upper panel: unit cell of the oxidized graphene; lower panel: electronic structures for the systems without spin and with the AFM and FM couplings. (a) and (b) are for the regular epoxy- and epoxy-pair-oxidized graphene, respectively.

graphene is AFM (or nonmagnetic), the energy difference is only 10 meV/edge carbon atom with respect to that in the FM coupling, indicating that the FM state can be thermally realized. For the epoxy-pair-oxidized graphene, however, its ground state shows FM coupling with the energy difference of 3 meV/edge carbon atom with respect to that in the AFM coupling (i.e., the nonmagnetic state).

4.4 Summary

In summary, the magnetic properties of ZGNR oxidized by epoxy-pair and single-epoxy chains are investigated. Our results show that the epoxy-pair chain can enhance the local spin moment of its nearest neighbors, leading to the finite total moment, even if there is AFM coupling across the two ribbon edges, which is in stark contrast with the vanishing total moment for ZGNR. In addition, depending on the position of the epoxy pair chain, the spin-resolved electronic structures are modified in such a way that they can undergo the transition from a half-metal to semiconductor via Fermi level tuning, regardless of AFM or FM coupling. Moreover, these properties are independent of the transverse electric field, which is a prerequisite for ZGNR to behave like a half-metal with AFM coupling or a semiconductor with FM coupling. The epoxy chain, however, has little impact on the magnetic and electronic properties of ZGNR. The findings here provide an avenue to manipulate the magnetic and electronic properties of ZGNR for future spintronic applications.
CHAPTER 5  GAS SENSING PROPERTIES OF

GRAPHENE-BASED NANOMATERIALS

The electrical conductance-based gas sensor works by monitoring the conductance change upon the adsorption of target gas molecules. Physically, the conductance depends on both the carrier concentration and the carrier mobility. Therefore, quantitative characterizations of the gas adsorption and carrier concentration and mobility are critical to understanding gas sensing process of any material. In addition, the sensitivity and selectivity of a gas sensor can be modified and tuned by fabricating hybrid structures of nanoparticles and graphene-based materials. In this chapter, we present in Section 5.1 a statistical thermodynamics model to calculate the gas adsorption density, and in Section 5.2 we present the van der Pauw and Hall measurements on thermally reduced graphene oxide (TRGO) thin films to extract the carrier concentration and the carrier mobility. Finally, the sensitivity enhancement through nanoparticle decoration on the RGO is presented in Section 5.3.

5.1 Modeling on the Gas Adsorption Density/Coverage

For the physical adsorption, gas molecules are attracted to the solid surfaces forming the adsorption layer. Depending on the gas concentration, it could be multilayer or monolayer adsorption. Usually, the Langmuir adsorption isotherm is used for monolayer adsorption to characterize the gas adsorption in terms of coverage (defined as the fraction of sites occupied). At low coverage, the spreading pressure of the adsorbed gas is equal to
its partial pressure before adsorption, and the coverage is linearly proportional to the pressure. Under this circumstance, the coverage could be reformulated in terms of per unit area and rephrased as density, which is also known as the Henry adsorption isotherm. When the gas concentration increases, the coverage will become nonlinear and asymptotic to unity. Here, we develop a statistical thermodynamics model to establish the Langmuir (or Henry) adsorption constant with inputs from DFT calculations.

Considering a single gas molecule approaching the solid surface in the free state as illustrated in Fig. 5.1, it will be trapped on the surface due to the attractive van der Waals force. For the homogeneous solid surfaces, the potential energy between the gas molecule and the solid surface can be regarded as independent of the adsorption sites across the surface defined in the xy plane. Thus, the interaction energy can be represented by the Morse potential only in the z direction as

$$V(z) = D_e \left[ e^{-2\gamma(z-z_e)} - 2e^{-\gamma(z-z_e)} \right],$$

(5.1)

where $D_e$ is the potential well depth, $z_e$ is the equilibrium distance between the gas molecule and the solid surface, $\gamma$ is the fitting parameter. All these three quantities can be found by fitting the distance-dependent interaction energy with the Morse potential in Eqn. (5.1). Solving the Schrödinger equation with the Morse potential, the eigenvalues of states are obtained as

$$E_n = -\hbar \omega_g \frac{\left[-2(2n+1)+8\Delta\right]^2}{64\Delta}, n = 1, 2, \ldots$$

(5.2)

in which $\omega_g = \gamma(2D_e/m_g)^{1/2}$ is the characteristic frequency of a gas molecule with mass $m_g$ and $\Delta$ is defined as $\Delta = D_e/\hbar \omega_g$. Here we assume both the adsorbed gas molecule and the free one have zero energy at infinity ($z = \infty$) to investigate the equilibrium
between them, and the gas molecule is considered to be adsorbed on the surface if the energy values are negative.

\[ V(\bar{z}) = D_e \left[ e^{-\gamma (\bar{z} - \bar{z}_e)} - 2e^{-\gamma (\bar{z} - \bar{z}_e)} \right] \]

Fig. 5.1 Schematic of the interaction between the gas molecule and the solid surface in the approximation of Morse potential as the gas molecule in the free state approaches the solid surface along the \( z \) direction with the potential well depth \( D_e \) and equilibrium distance \( \bar{z}_e \) illustrated. The gas molecule is considered to be adsorbed onto the solid surface when its vibrational energy \( E_n \) is negative.

In the framework of equilibrium approach, the energies of the adsorbed gas molecules follow the Boltzmann distribution and the movements of molecules among the energy levels inside the potential well are treated as a random walk process. For monolayer gas adsorption with low coverage, the energy levels near the bottom of the potential well are mostly occupied. Therefore, it is reasonable to treat the gas molecules as harmonics oscillators. Also, the adsorbed gases can be considered to be mobile across the surface.
plane at high temperatures owing to the low energy barrier of the homogeneous surface.

Then the canonical ensemble partition function for a single adsorbed gas molecule is only related to the temperature as \[^{243}\]

\[
q(T) = \frac{A}{\lambda^2} \exp\left(\frac{D_e}{k_B T}\right) \sum_n \exp\left(-\frac{E_n}{k_B T}\right),
\]

(5.3)

where \(A\) is the solid surface area and \(\lambda = (2\pi \hbar^2 / m g k_B T)^{1/2}\) is the thermal wavelength of the gas molecule. The total number of the adsorbed gas molecules is

\[
N = P_g q \exp\left(\frac{\mu_0}{k_B T}\right),
\]

(5.4)

with \(P_g\) the partial pressure of target gas and \(\mu_0\) the standard chemical potential. With the approximation of an ideal gas by neglecting the interactions between adsorbed gas molecules with a low concentration, \(\mu_0\) is found to be \(k_B T \ln(\lambda^3 / k_B T)\). Thus, we can obtain the gas adsorption density \(n_g\) from Eqns. (5.3) and (5.4) as

\[
n_g = \frac{N}{A} = \frac{P_g \lambda}{k_B T} \exp\left(\frac{D_e}{k_B T}\right) \sum_n \exp\left(-\frac{E_n}{k_B T}\right),
\]

(5.5)

To adopt Eq. (5.5) to predict the gas adsorption density, we need the Morse potential from the theoretical inputs. The DFT calculations were carried out by the code OPENMX\[^{144}\]. The pseudo atomic orbitals (PAOs) were used to expand the single electron wavefunction and were specified by X7.0-s\(^2\)p\(^2\), where X stands for the elements of H, C, N and O, 7.0 represents the cutoff atomic radius in Bohr and s\(^2\)p\(^2\) indicates that the basis functions are expanded by two primitive orbitals of individual s and p orbitals, respectively. Norm conserving pseudopotential was used with the treatment of an exchange-correlation functional in the formalism of GGA-PBE \[^{155}\] for CO and NH\(_3\) without spin and for NO and NO\(_2\) with spin polarizations. The 3×3 supercell composed by the centered rectangular unit cell of graphene and the layer spacing larger than 20 Å
were used for the single gas molecule adsorption so that the interactions could be ignored between the adjacent layers and between the molecules themselves due to the periodic

\[ R = \frac{n_s \text{-} n_s^{'}}{n_s} \times 100\% \]

Fig. 5.2 The characteristics of CO, NO, NH₃ and NO₂ adsorption on graphene and RGO. (a) The exact (estimated) gas adsorption densities \( n_s \) (\( n_s' \)) on graphene with the relative error \( R \) shown in the inset; (b) Upper panel: the exact (estimated) gas adsorption coverage
θ (θ') for ether and carbonyl in RGO, respectively; Lower panel: the relative error $R$ for ether and carbonyl.

boundary conditions. The numerical integrations were performed with the cut-off energy of 2,720 eV in real space and the k-point density of 0.02/Å in the reciprocal space. The structural relaxations were terminated with the force criteria of 0.01 eV/Å.

Despite its great success in predicting many properties of solids and molecules, one drawback of the Kohn-Sham DFT is its failure in describing the long range electron-electron correlations that give rise to the van der Waals force (i.e., the attractive dispersion force) responsible for the weak interactions among molecules and solids. Generally, the common GGA functionals would severely underestimate this long range correlation and this problem still exists even for the hybrid functionals by replacing part of the local with nonlocal Hartree-Fock exchange term. For the gas adsorption systems considered here, it is significant to include this van der Waals force to faithfully quantify the adsorption density or coverage. To realize this, we adopted the modified version of the DFT-D method in the semiempirical GGA functional to incorporate this dispersion force using the damped atom pairwise dispersion corrections in the form of $C_6 \cdot R^{-6}$, which has been shown to be very successful in describing the medium to large range interactions.

Fig. 5.2 (a) shows the predicted adsorption density of CO, NO, NH$_3$ and NO$_2$ on graphene. As we can see, the adsorption densities of CO ($0.13 \times 10^9$ cm$^{-2}$), NO ($0.87 \times 10^{10}$ cm$^{-2}$) and NH$_3$ ($0.62 \times 10^9$ cm$^{-2}$) are close to each other, while that of NO$_2$ ($0.99 \times 10^{12}$ cm$^{-2}$)
is strikingly greater by about 2 to 3 orders of magnitude. The substantially enhanced adsorption density for NO$_2$ is largely attributed to its deeper potential well depth or higher binding energy of 0.214 eV compared with 0.086 eV for CO, 0.147 eV for NO, and 0.112 eV for NH$_3$, since the occupying number of oscillators in the Boltzmann distribution will grow drastically with the increased energy. We could also project the predicted adsorption densities into the primitive cell of graphene, which are 0.25×10$^{-8}$/cell, 0.17×10$^{-6}$/cell, 0.12×10$^{-7}$/cell and 0.19×10$^{-4}$/cell for CO, NO, NH$_3$ and NO$_2$, respectively, suggesting the dilute adsorption. Because of its homogeneous surface, these gas species have been shown to possess similar binding energy on different adsorption sites (top, bridge and hollow)$^{134,138}$, namely, low migration energy barriers. Thus, the use of Eqn. (5.5) to calculate the adsorption densities for these gases is reasonable.

Experimentally, the hole concentration induced by NO$_2$ (1 ppm) adsorption on graphene$^{126}$ has been measured to be around 0.5×10$^{11}$ cm$^{-2}$. Each NO$_2$ molecule can attract about 0.14 e from graphene by the Mulliken charge analysis in our calculation and about 0.099 e by the Hirshfeld charge analysis$^{134}$. Thus, the adsorption density of NO$_2$ is estimated to be around 0.42×10$^{12}$ cm$^{-2}$. Although our prediction of the adsorption density of NO$_2$ is close to the experimental value, we should be aware that the small discrepancy could stem from the following respects. On one hand, the DFT calculations, even with the treatment of the dispersion force, only can approach the exact adsorption energy of the adsorbates on surfaces (the slight overestimation or underestimation will not be avoided). On the other hand, the calculations were carried out at 0 K, which would also give rise to slight overestimation of gas adsorption energy compared with the case that sensors are
practically operating around room temperature. Moreover, the effects of molecule rotations and intramolecular vibrations on the adsorption are neglected, leading to the increased adsorption probability of gas molecules approaching the surface.

Since graphene is mostly sensitive to NO\textsubscript{2} and reluctant to CO, NO and NH\textsubscript{3} as demonstrated above, it is intriguing to structurally modify graphene and design new gas sensors toward these three insensitive gases. RGO can be used for gas sensing by tuning its oxygen content by controlling the reduction conditions and it also has the larger surface-to-volume ratio. Despite the fact that main functional groups in GO are epoxide and hydroxyl, the remaining oxygen atoms in RGO are in the forms of ether and carbonyl\textsuperscript{177}. Therefore, we also consider here the effects of these two functional groups inside the carbon plane on the gas sensing.

Note that Eqn. (5.5) holds for the homogeneous surfaces and when the gas molecules are dilute and mobile. For the nonhomogeneous surfaces with distinct adsorption sites, the gas molecules are inclined to be localized to the sites with the largest binding energy. Strictly speaking, Eqn. (5.5) would fail under this circumstance. However, the generalized Langmuir equation can be alternatively adopted to estimate the coverage \(\theta_i\) of different types of adsorption sites at equilibrium as opposed to the adsorption density of the homogeneous surface. The total coverage \(\theta\) is

\[
\theta = \sum_i \alpha_i \theta_i = \sum_i \alpha_i \frac{K_{e,i}C_g}{1 + K_{e,i}C_g},
\]

\[
K_{e,i} = \frac{K_{a,c}}{K_{d,e}} = \frac{1}{\omega_g} \left( \frac{2\pi k_B T}{m_g} \right)^{1/2} \exp \left( \frac{D_{e,i}}{k_B T} \right),
\]

(referenced equations)
and \( C_g = \frac{P_g}{P_{air} + P_g} C_{air} \). (5.8)

Here \( \alpha_i \) stands for the fraction of adsorption site \( i \) with the potential well depth of \( D_{e,i} \), \( K_{e,i} \) is the equilibrium constant, \( P_{air} \) is the air pressure and \( C_{air} \) is constant with the value of \( 2.9 \times 10^8 \) m\(^{-1} \) for air at room temperature. As \( K_{e,i} \) is independent of the state of gas (classical vs. steady state vs. equilibrium), we can define it as the ratio of the classical adsorption rate constant \( K_{a,c} = (k_B T / 2\pi m g)^{1/2} \) to the classical desorption rate constant \( K_{d,c} = \omega_g \exp \left(-\frac{D_e}{k_B T} \right) / 2\pi \). Using the definition of \( \omega_g \), Eqn. (5.7) can also be formulated as

\[
K_{e,i} = \frac{\sqrt{\pi}}{\gamma_i} \frac{k_B T}{D_{e,i}} \exp \left(\frac{D_{e,i}}{k_B T} \right). \quad (5.9)
\]

Fig.5.2 (b) shows coverage of CO, NO, NH\(_3\) and NO\(_2\) on the RGO with ether, carbonyl and epoxide. For ether, the coverage is \( 0.17 \times 10^{-5} \), \( 0.84 \times 10^{-5} \), \( 0.72 \times 10^{-4} \) and \( 0.84 \times 10^{-3} \) for CO, NO, NH\(_3\) and NO\(_2\), respectively, for carbonyl, the coverage is \( 0.12 \times 10^{-5} \), \( 0.22 \times 10^{-2} \), \( 0.42 \times 10^{-3} \) and \( 0.35 \times 10^{-5} \) for CO, NO, NH\(_3\) and NO\(_2\), respectively. Epoxide can only physically attract CO, NH\(_3\) and NO\(_2\) with coverage of \( 0.29 \times 10^{-5} \), \( 0.78 \times 10^{-5} \) and \( 0.79 \times 10^{-6} \), while NO will react with epoxide-forming NO\(_2\). Hence, ether in RGO can greatly enhance the sensitivity to NH\(_3\) and NO\(_2\) and carbonyl in RGO can greatly enhance the sensitivity to NO and NH\(_3\). However, epoxide is less attractive to NO\(_2\). In addition, NO will bond with the oxygen atom in epoxide to form NO\(_2\) and then adsorb on the underlying carbon plane in a way similar to the adsorption of NO\(_2\) on graphene. As epoxide groups tend to aggregate together\(^{248}\), NH\(_3\) is physically adsorbed in the epoxide-rich region as considered here. However, it was also shown that NH\(_3\) can be dissociated
by single epoxide into the OH and NH₂ species. The increased coverage of NH₃ on both ether and carbonyl is due to the H bond between the H atoms in NH₃ and O atoms in the functional groups. Nonetheless, the enhanced coverage of NO results from the trend to form the NO₂ complex between the NO molecule and the carbonyl group. NO₂ is attracted to ether with oxygen atoms pointing to it, unlike the NO₃ complex between NO₂ and carbonyl on the edge of RGO or between NO₂ and metal oxide surfaces. These results suggest that RGO can be a good candidate for gas sensing toward NO, NH₃ and NO₂, consistent with the experimental observations.

Note that two parameters \( D_e \) and \( E_n \) in Eqn. (5.5) and \( D_e \) and \( \gamma \) in Eqn. (5.9) are required to obtain the adsorption density and coverage, respectively. The potential well depth \( D_e \), equivalent to the binding energy of a single gas molecule on the solid surface, can be determined experimentally or theoretically. The energy level \( E_n \) and the fitting parameter \( \gamma \), however, can only be obtained by fitting the Morse potential and then solving the Schrödinger equation with it. For practical purposes, it is convenient to estimate the gas adsorption density or coverage without resorting to fitting the Morse potential and solving the Schrödinger equation. To this end, it is found that Eqns. (5.5) and (5.9) can be reformulated by removing \( E_n \) and \( \gamma \) as

\[
n_g' \sim \frac{5}{2} \frac{P_{g \lambda}}{k_B T} [\exp \left( \frac{D_e}{k_B T} \right)]^2 \tag{5.10}
\]

and

\[
K_{e,i}' \sim \frac{6}{5} \sqrt{\frac{k_B T}{D_{e,i}}} \exp \left( \frac{D_{e,i}}{k_B T} \right) \times 10^{-10} \text{ m} \tag{5.11}
\]

Consequently, the estimated adsorption densities from Eqn. (5.10) are also presented in Fig.5.2 (a). Compared with the exact values from Eqn. (5.5), we can see that the absolute
discrepancies are around 15% and are less than 23% even for NH₃ which has the largest value. It can also be seen from Fig. 5.2 (b) that the estimated coverage values by plugging Eqn. (5.11) into Eqn. (5.7) are nearly equal to the exact values for NO adsorbed on carbonyl and NO₂ on ether. Although CO has the largest relative error (~12%) despite its rather small coverage when it approaches carbonyl, the errors are within ± 8% for all other gases. Thus, we can conclude that the ratio of the potential well depth $D_e$ to the binding energy can solely be used to determine the adsorption density and the coverage with high accuracy.

As stated above, gas molecules generally are adsorbed to the surface with negative energy values. For a low concentration of gas molecules and abundant adsorption sites, the mutual interactions between the adsorbed molecules can be neglected since the molecular distance is quite large. Thus, the adsorption density should be governed by the gas concentration for the same type of solid surface, e.g., graphene as we consider here, and is irrespective of the magnitude of the potential well depth. But this is clearly not the case as expected and as shown above for the four target gases. In essence, this originates from the fact that not every individual incoming gas molecule can be attracted to the solid surface, taking into account the thermal fluctuations of both gas molecules and the solid surface as reflected in the Boltzmann factor in Eqns. (5.5), (5.9), (5.10) and (5.11). Alternatively, we could understand this effect in terms of the thermally averaged sticking coefficient of gas molecules approaching the solid surface, which is derived as the implicit function of adsorption energy $\epsilon$:

$$< s >_T = \text{erf}(\beta) \left\{ 1 - \left[ \frac{2\beta^2 [1 - \text{erf}(\beta)] - 4\beta^2 e^{-\beta^2}}{\text{erf}(\beta)} \right]^2 \right\}$$  \hspace{1cm} (5.12)
where \( \beta = \frac{1}{2} \sqrt{\ln \left( \frac{1}{\zeta} \right) \left( \frac{1-\zeta}{1+\zeta} \right)} \) and \( \zeta = \exp \left( -\frac{\Delta \epsilon}{k_B T} \right), \Delta \epsilon \in [0, D_e] \). The resulting room temperature sticking coefficients with respect to the adsorption energy for gas molecules CO, NO, NH\(_3\) and NO\(_2\) on both graphene and RGO are also illustrated in Fig. 5.3. We can see that the sticking coefficient increases and saturates to unity at a higher energy. This is expected since the higher the adsorption energy, the less likely that the gas molecule bounce off the surface due to the thermal vibrations of the surface atoms. Classically, the adsorption rate constant is the arriving rate of gas molecules of \((k_B T/2\pi m_g)^{1/2}\) regardless of the adsorption energy.

Fig. 5.3 Color-coded regions of sticking coefficient <s> with respect to the potential well depth \( D_e \) for CO, NO, NH\(_3\) and NO\(_2\) adsorption on graphene and ether and carbonyl in RGO. The right line in each region indicates the upper bound of the potential well depth \( D_e \).
Pagni and Keck\textsuperscript{247} have shown that both the steady state and the equilibrium adsorption rate constants increase with respect to the adsorption energy, and both are greater than their classical counterparts at the higher adsorption energy, although the critical energy depends on the masses and the characteristic frequencies of both gas molecules and surface atoms at the adsorption sites. When the upper limit is specified for each gas, in contrast to the adsorption of NO\textsubscript{2} on graphene, CO, NO and NH\textsubscript{3} have smaller coefficients due to their weaker physical binding to graphene. However, the situations are quite different for adsorptions on ether and carbonyl in RGO. While NO and NH\textsubscript{3} possess enhanced sticking coefficients when attracted toward both of them, CO and NO\textsubscript{2} are only more attractive to ether. These results are coherently consistent with the analyses based on adsorption density and coverage.

Note that Eqns. (5.5) and (5.6) would fail in the case of multilayer adsorption, in which the adsorbed gas with pressure higher than its partial pressure in the free state is in the compressed phase and cannot be treated as the ideal gas. Future work can be done to derive the gas pressure for the imperfect gas in the adsorption layer thermodynamically. Then Eqn. (5.8) can be applied to determine the adsorption density by replacing the partial pressure $P_g$ with the compressive pressure. And the Brunauer-Emmelt-Teller equation should be used instead of Eqn. (5.6) to estimate the coverage.

In summary, the interactions between monolayer gas molecules and solid surfaces have been investigated for gas sensing applications. Depending on whether gas molecules can be mobile on the homogeneous surfaces or localized to certain adsorption sites on the
nonhomogeneous surfaces (which are usually located at imperfections like the defects and edges along the material or the micropores within it), statistical thermodynamic models are developed to characterize the monolayer gas adsorption density and coverage, respectively. With inputs from the first-principles calculations, we studied the adsorptions of four target gas species CO, NO, NH₃ and NO₂ on the homogeneous graphene and nonhomogeneous RGO surfaces. Our results show that graphene is more sensitive to NO₂, while NO (NO₂) prefers to be attached to carbonyl (ether) in RGO. In addition, NH₃ can be moderately attracted to both graphene and RGO, whereas CO shows a very weak attraction for both surfaces. Although the derived analytical expressions require first fitting the Morse potential and solving the Schrödinger equation, we found that the adsorption density and coverage can be effectively estimated by the binding energy of a gas molecule alone with high accuracy. This is desirable and significant since the binding energy can be determined either experimentally or theoretically. Within our knowledge of a literature survey on the experimental data, we could only obtain the experimentally extracted adsorption density for NO₂ on graphene \( (0.42 \times 10^{12} \text{ cm}^{-2}) \) \(^{126}\), close to our prediction \( (0.99 \times 10^{12} \text{ cm}^{-2}) \). Our proposed approaches to quantify the monolayer gas adsorption in terms of density on a homogeneous surface and coverage on a nonhomogeneous surface offer solid evidence to assess the performance of gas sensing on a quantitative ground. Our approach also provide a means to understand and even determine the gate voltage required to enhance the gas sensitivity (or recovery rate but with the sign of the voltage reversed), which varies the gas surface interaction strength. Moreover, our approach help to identify the contributions from distinctive types of adsorption sites that are important in tailoring the gas sensing performance through
structural modification (e.g., the contributions of functional groups in RGO can be obtained by their individual species concentration as determined by microscopic techniques and the calculated gas adsorption coverage toward a specific gas).

5.2 van der Pauw and Hall Measurements on TRGO Thin Films

In this section, van der Pauw and Hall measurements are performed on the TRGO films obtained at various temperatures to quantify changes in the sheet resistance, carrier concentration, and carrier mobility before and after exposure to gases. We first consider the scenario that GO thin films with the same thickness are thermally reduced in the Ar atmosphere for 2 hours at three different temperatures: 250 °C (S1), 300 °C (S2) and 350 °C (S3). For all the three samples, the measured sheet resistance decreased upon NO\textsubscript{2} adsorption as shown in Fig. 5.4 (a). We can also see that the higher the reduction temperature, the lower the sheet resistance. The positive signs of the sheet carrier density of samples S1 to S3, shown in Fig. 5.4(b), indicate that RGO thin films act as p-type semiconductors, since the vacancies due to the release of CO and CO\textsubscript{2} molecules in the reduction process and edge C atoms are occupied by O\textsubscript{2} molecules in the air, leading to charge transfer from the carbon plane into the adsorbed O\textsubscript{2} molecules. Upon exposure to the NO\textsubscript{2} atmosphere, the carrier density further increases, suggesting that NO\textsubscript{2} molecules attract electrons from the RGO, in good agreement with its oxidizing nature. Generally, there are three types of adsorption sites on RGO. First, just like pristine graphene, NO\textsubscript{2} molecules sit above the sp\textsuperscript{2} C atoms with the O atoms pointing outwards;
second, it can form the NO₃ complex when the NO₂ molecule is bound to the remaining oxygen atoms in the epoxide groups; third, it interacts with the O₂ molecules attached at the C vacancies. Fig. 5.4 (c) clearly shows that the Hall mobilities of carrier decrease upon the NO₂ adsorption.
Fig. 5.4 van der Pauw and Hall measurements on RGO thin films before and after NO$_2$ adsorption. (a) sheet resistance, (b) sheet carrier density, (c) carrier Hall mobility, and (d) absolute values of relative changes for the quantities shown in (a) to (c).
The decrease in mobility arises mainly from the scattering of carrier transport in the C plane by the adsorbed NO₂ molecules. Note that the derived Hall mobilities are smaller than the reported values in the literature which vary from 1.5-200 cm²V⁻¹s⁻¹.²⁵⁴-²⁵⁶ This variation is likely due to two factors. First, the sample thickness and the reduction temperature are different, and thus the measured results are closely related to the individual sample; second, it also depends on how well the RGO flakes connect to each other since the measurements are for the overall thin films rather than individual flakes.

To quantitatively compare the

| TABLE 5.1 Summary of van der Pauw and Hall measurements on different samples. |
|---|---|---|---|---|
| | TRGO thin films | Sheet resistance (kΩ/□) | Sheet carrier density (×10¹⁴cm⁻²) | Hall mobility (cm²V⁻¹s⁻¹) |
| Sample | Thickness (µm) | Reducing Temperature(°C) | Air | NO₂ | Air | NO₂ | Air | NO₂ |
| S1  | 100-150 | 250 | 199.63 | 184.65 | 0.52 | 0.71 | 0.60 | 0.48 |
| S2  | 300 | 35.02 | 31.58 | 3.03 | 3.48 | 0.65 | 0.57 |
| S3  | 350 | 25.22 | 23.99 | 3.77 | 6.20 | 0.66 | 0.42 |
| S4  | 400-500 | 275 | 84.70 | 83.67 | 0.51 | 0.99 | 1.45 | 0.76 |
| S5  | 250-350 | 450 | 18.78 | 18.47 | 3.57 | 5.17 | 0.93 | 0.65 |

variation before and after the gas adsorption, absolute values of the relative changes of sheet resistance, carrier density, and Hall mobility are presented in Fig. 5.4(d). It can be seen that the changes in sheet resistance are the smallest, suggesting that measuring resistance is not the most judicious choice to gauge the sensitivity of RGO samples for...
detecting NO₂. Instead, both variations in carrier density and in mobility are more pronounced and they could be used as effective signals for the design of novel and highly sensitive gas sensors.

Fig. 5.4 also presents the results from samples S4 and S5, which had different film thicknesses and were reduced at different temperatures than samples S1-S3. The trends of variations in the resistance, charge density, and mobility are consistent with those of samples S1 to S3, indicating that the conclusions drawn above for samples S1-S3 also hold for samples S4- S5. Thus, we can conclude that it is intrinsic to RGO thin film-based gas sensors for detecting NO₂ that the gas molecules induced variation in carrier density contribute more than the variation in the mobility to the variation in the sheet resistance of the films. Such a conclusion is independent of the films thickness, reduction temperature, and the connectivity between individual RGO flakes.

5.3 Gas Sensitivity Enhancement by Nanoparticle Decoration on RGO

Generally, hybrid structures can be adopted to enhance the sensitivity with each component functioning differently. For example, C-based nanomaterials like graphene or nanotubes are more sensitive to NO₂ than NH₃. To enhance the sensitivity of NH₃ and the detection limit of NO₂, Cui et al. ¹³⁵ fabricated the multiple hybrid nanosensors with structures of MWCNTs/SnO₂/Ag and MWCNTs/Ag, respectively, and found that Ag
nanoparticles significantly improve the sensitivity of both NO$_2$ and NH$_3$, while the SnO$_2$ nanoparticle only enhances the sensitivity towards NO$_2$.

To understand the roles of these nanoparticles, we performed DFT calculations of gas adsorption using the FLAPW method as implemented in flair$^{187}$ using the GGA of PBE$^{155}$. The cutoff energy of the plane wave basis was 435 eV. Despite the fact that multiple facets exist in the actual sensing system, only those theoretically stable are considered here to gain a sense of their respective roles. To model the local electronic and structural properties associated with the adsorption of molecules on the predominant low surface energy facets of nanoparticles, periodic slab geometries were used. The (111) surface of Ag NPs was simulated by the slab model of 4 layers of atoms in the $\sqrt{3} \times \sqrt{3}$ super cell with an 8×8×2 k-point grid and a sphere radius of 2.5a$_B$, while the (110) surface of tin dioxide was represented by a 7-layer slab model in a 1×2 cell with a 4×4×4 k-point grid and sphere radii of 2.5a$_B$ for Sn and 1.3a$_B$ for O. The vacuum region was kept above 12 Å for both models. The lattice parameters for the slabs were used from the relaxed bulk materials with 4.15 Å for Ag and 4.943×3.337 Å for SnO$_2$, somewhat larger than the experimental values of 4.10 Å and 4.737×3.186 Å, as expected for GGA. The sphere radii for the gas molecules were 1.0a$_B$ for both N and O and 0.6a$_B$ for H. The 2 uppermost layers of atoms were relaxed before gas adsorption; subsequently, the topmost layers of atoms and gas molecules were allowed to fully relax during the adsorption. The force criterion for the optimization was within 0.04 eVÅ$^{-1}$. The following models were considered here. To address the issue of surface oxidation of Ag, as expected when the NPs are exposed to air, a monolayer coverage of O on Ag(111) (AgO in the surface) was
considered. Similarly, both the planar-reduced and unreduced (110) surfaces were considered for SnO$_2$.

DFT calculations were performed for NO$_2$ adsorption on the Ag (111) surface terminated with an epitaxial monolayer of AgO (111) in normal fcc stacking, as shown in the atomic model in Fig. 5.5(a). There are three possible high symmetry sites for NO$_2$ adsorption on this surface: (1) on top of oxygen; (2) on top of silver; and (3) in 3-fold hollow site. The lowest energy configuration is obtained when NO$_2$ adsorbs atop the oxygen ion with N pointing downwards, as illustrated in the top-view atomic model in Fig. 5.5(a). Fig. 5.5(b) shows the top-view atomic structure of the most stable adsorption scenario for NH$_3$.
obtained from our DFT calculation for the epitaxial AgO (111) monolayer on Ag(111).

Fig. 5.5 Upper panel: top view of gas adsorption on the oxidized silver(111) surface (AgO). (a) NO$_2$ is attracted to O$^{5-}$ forming an NO$_3$ $^{5-}$ complex. (b) NH$_3$ sits above the hollow site with the nitrogen atom pointing up. Lower panel: charge density difference upon gas molecule adsorption on the AgO surface. Green and yellow represent electron accumulation and depletion regions, respectively. (c) NO$_2$ acts as an acceptor with a net electron gain of 0.024 e$^-$. (d) NH$_3$ works as a donor with a net electron loss of 0.004 e$^-$. 
NH$_3$ is adsorbed above the hollow region, with H atoms pointing downwards and attracted to Ag atoms. Fig. 5.5(c) shows a side view of the charge redistribution upon NO$_2$ adsorption above the surface oxygen ion. This demonstrates that the charge density of both the pz orbitals of oxygen atoms in NO$_2$ and the Px,y orbitals of oxygen atoms on the AgO surface increases upon adsorption; meanwhile, the charge density of the pz orbital of oxygen on silver and the region between the NO$_2$ molecule and the surface decreases. Hirshfeld charge analysis suggests that the charge has been transferred from silver (-0.07 e) to surface oxygen (+0.05 e) and further into the target gas molecules (+0.024 e), while each oxygen atom gains 0.02 e and each nitrogen atom loses 0.015 e in NO$_2$. The charge density difference of NH$_3$ adsorbed on the oxidized Ag surfaces (sideview in Fig. 5.5(d)) indicates that charges could be transferred from H atoms to Ag and further to O on the silver surface. The analysis of the charge density shows that each H atom in NH$_3$ loses 0.003 e, while each N atom gains 0.005 e. Overall, the entire molecule loses 0.004 e.
Fig. 5.6 Upper panel: Perspective views of the SnO$_2$ (110) surface with the coordination number of different Sn atoms labeled, (a) planar-reduced surface and (b) oxidized surface with oxygen atoms sitting on the bridge sites. Lower panel: Charge density difference upon NO$_2$ molecule adsorption on the surface. Green and yellow represent electron accumulation and depletion regions, respectively. (c) NO$_2$ is attracted directly to the Sn4 atom with a gain of 0.0576 e$^-$. (d) NO$_2$ forms NO$_3$ complex with a gain of 0.0069 e$^-$. For NH$_3$ adsorption, it prefers the Sn5 site instead of the bridging oxygen. However, this site is preoccupied by O$_2$ at room temperature and leads to the reluctance of the sensor to NH$_3$. 
To further investigate the role of the oxygen coverage level on the Ag surface, we considered NH$_3$ adsorption on a clean Ag surface and Ag$_3$O surfaces in DFT calculations, then compared with the results for AgO. The results showed that NH$_3$ is in favor of sitting above the Ag site with a binding energy of 0.40 eV on the clean Ag surface. For Ag$_3$O, the hollow site is preferable while the binding energy increases to 0.74 eV, as opposed to the oxygen site forming a hydrogen bond with binding energy of 0.15 eV. Therefore, NH$_3$ is attracted to the unoxidized region at a low oxygen coverage level. The N atom is pointing to Ag in both cases, which is different from AgO where the three H atoms are pointing towards the surface. On the AgO surface, however, the NH$_3$ binding energy decreases to 0.36 eV in the lowest energy configuration, as shown in Fig. 5.4 (b). Hirshfeld charge analysis shows that NH$_3$ adsorbed on the clean and Ag$_3$O surfaces gains 0.886 e and 0.015 e, respectively, suggesting that NH$_3$ acts as an acceptor, contrary to what we observed in our experiment$^{130}$. Therefore, a fully oxidized Ag surface (AgO) is the practical case in our sensor, and oxygen atoms could easily migrate on an AgO surface because of the low barrier height of 0.32 eV.

Previous calculations$^{257}$ regarding the adsorption mechanism on the SnO$_2$ surface have shown that NO$_2$ forms stable NO$_3$ groups on the (10̅1) and (010) surfaces of SnO$_2$ nanoribbons from room temperature up to 700 K. Among the low-index surfaces, the (110) surface is the most stable, as it has the lowest surface energy, followed by the (010) and (101) surfaces. Since our SnO$_2$ nanoparticles homogenously crystallized in the gas phase, the (110) surface is expected to be predominant. Since oxygen vacancies are common (constituent) defects on oxides surfaces, we performed calculations on both the planar reduced and unreduced (stoichiometric) SnO$_2$ (110) surfaces to address the issue
of NO₂ sensing as shown in Fig. 5.6 (a) and (b), respectively. For the unreduced surface, NO₂ favors the formation of an NO₃ complex with a binding energy of 1.76 eV. For the reduced surface, NO₂ favors bonding with Sn4. Charge analysis (based on charges in the atomic spheres) shows small charge transfers from the Sn4 atom to the adsorbed NO₂ molecule of 0.06 e and 0.01 e for the reduced and unreduced surfaces, as shown in Fig. 5.6 (c) and (d), respectively. However, the surface oxygen on the unreduced SnO₂ surface gains ~0.50 e (within the oxygen sphere) upon NO₂ adsorption, effectively forming a negatively charged NO₃ cluster. Hence, the adsorbed surface oxygen found on SnO₂ exposed to air at room temperature plays a significant role in enhancing the performance of the sensor towards NO₂.

It is well known that pure CNTs are sensitive to NH₃ based on both theoretical predictions and experimental observations. Nevertheless, the insensitivity of SnO₂ to NH₃ at room temperature is not fully understood and few studies have been carried out. Our calculation indicate that NH₃ prefers bonding to the Sn5 site irrespective of whether surface oxygen atoms are on the SnO₂ (110) surface or not. The binding energies are 0.53 eV and 1.27 eV for reduced and unreduced surfaces, respectively. However, these Sn5 sites have been shown to be strongly preoccupied by oxygen molecules at room temperature, with a binding energy of 1.2 eV in our calculation. This energy is quite large and oxygen molecules could not be desorbed at room temperature, resulting in weak attraction to NH₃ at Sn5 sites. Thus, SnO₂ is insensitive to NH₃ at room temperature.

In summary, we calculated the NH₃ and NO₂ adsorption on crystalline Ag with oxidized surface layer and SnO₂ nanoparticles. The results show that Ag is sensitive to both gas
species, while SnO\textsubscript{2} can mainly adsorb NO\textsubscript{2}. The insensitivity of SnO\textsubscript{2} to NH\textsubscript{3} is due to the fact that the attraction sites on SnO\textsubscript{2} are occupied by oxygen molecules in air at room temperature. Moreover, NO\textsubscript{3} complex forms when the NO\textsubscript{2} molecule is adsorbed on both the surface-oxidized Ag and planar-unreduced SnO\textsubscript{2} (110) surface.

5.4 Summary

In this chapter, statistical thermodynamics models are used to analytically characterize the monolayer gas molecule adsorption on solid surfaces in terms of density and coverage for mobile and localized adsorptions, respectively, which is critical for gas sensing applications. By testing the monolayer adsorption of CO, NO, NH\textsubscript{3} and NO\textsubscript{2} gas molecules on graphene and RGO, we found that the adsorption density and coverage can be estimated from the binding energy of gas molecules alone with high accuracy compared with the exact values obtained by solving the Schrödinger equation. The proposed approaches to quantitatively characterize gas adsorption on solid surfaces are of great significance to help understand and optimize the performance of gas sensors. In addition, van der Pauw and Hall measurements of TRGO thin films suggest that the carrier concentration change is more dominant than the carrier mobility upon the gas adsorption. Finally, the insensitivity of C-based materials towards NH\textsubscript{3} can be enhanced by decorating them with Ag nanoparticles, while both Ag and SnO\textsubscript{2} nanoparticles will enhance the sensitivity toward NO\textsubscript{2}. 
CHAPTER 6 GAS SENSING PROPERTIES OF BLACK PHOSPHORUS THIN FILMS

The tunable bandgap of black phosphorus (BP) with respect to the layer numbers/film thickness makes BP attractive for gas sensor applications, and first-principles studies\(^{116}\) have shown that monolayer phosphorene exhibits superior sensing performance even better than graphene and MoS\(_2\). Experimentally, BP thin film-based gas sensors have been shown to be highly sensitive toward NO\(_2\) with a lower detection limit down to 20 ppb at room temperature\(^{260}\). In addition, the experimentally observed sensitivity is dependent on the film thickness\(^{260}\), even for the relatively thick film that is bulk-like. However, BP thin film-based gas sensors must be kept in dry air since water molecules will lead to the oxidization of BP. Thus, it is critical to understand how oxidation will affect the sensitivity. In this chapter, the gas adsorption density on BP will be analyzed from the DFT calculations presented in Section 6.1.1 and the analytical modeling for sensitivity will be established by considering the film thickness in Section 6.1.2. The theoretical and experimental characterizations of the sensor performance of oxidized BP will be presented in Section 6.2.

6.1 DFT and Statistical Thermodynamics Modeling on the Superior Sensitivity

6.1.1 Gas Adsorption Density on Monolayer Phosphorene

To elucidate the underlying mechanism of superior sensitivity, DFT calculations were performed using the code OPENMX\(^{261}\). The electron wavefunctions were expanded by
the pseudo atomic orbitals (PAOs) and specified by P7.0-\(s^2p^2d^1\), S7.0-\(s^2p^2d^1\), C5.0-
\(s^2p^2d^1\), N5.0-\(s^2p^2d^1\), O5.0-\(s^2p^2d^1\), and H5.0-\(s^2p^2\) for P, S, C, N, O, and H, respectively, 
where 7.0(5.0) represents the cutoff atomic radius in Bohr and \(s^2p^2d^1\) indicates that the 
basis functions are expanded by two primitive orbitals of individual \(s\) and \(p\) orbitals and 
one primitive orbital of individual \(d\) orbital. The core electrons were treated by the norm-
conserving pseudopotential with the exchange-correlation functional in the framework of 
GGA-PBE\textsuperscript{155} with and without spin polarization for NO\(_2\) and other gases (CO, H\(_2\), H\(_2\)S), 
respectively. The modified version of the DFT-D method\textsuperscript{245} in the semiempirical GGA 
functional was adopted to incorporate the van der Waals force in the gas adsorption 
systems considered here using the damped atom pairwise dispersion corrections in the 
form of \(C_6 \cdot R^{-6}\), which has been shown to be very successful in describing the medium- 
to large-range interactions\textsuperscript{246}. The numerical integrations were performed with a cut-off 
energy of 2,720 eV in real space and a k-point directional density of 0.02/Å in the 
reciprocal space. The structural relaxations were terminated with the force criteria of 
0.01eV/Å. A layer spacing larger than 20 Å was used for the single gas molecule 
adsorption so that suspicious interactions could be ignored between the adjacent layers 
and between the molecules themselves due to the periodic boundary conditions. The 
transition barrier was identified using the nudged elastic band (NEB) method\textsuperscript{262}. The \(k\)-
projected band structures were implemented by flair\textsuperscript{187} using the full-potential linearized-
augmented plane-wave method with the valence electrons treated by GGA. The 2D 
experimental lattice constants of BP (\(a=3.314\text{Å}, b=4.376\text{Å}, c=5.25\text{Å}\)) were used\textsuperscript{263}. 

Fig. 6.1 DFT calculations of NO₂ adsorption on phosphorene surface. (a) Top view of the adsorption of a single NO₂ molecule on the phosphorene surface with the oxygen atoms pointing downwards. (b) Side views of difference charge density contour plot \( (1.25 \times 10^{-3} \text{ electron/Bohr}^3) \) for the spin-up (left) and spin-down (right) states with the Mulliken charge transfer indicated. The violet and cyan color-coded regions indicate the charge accumulation and depletion, respectively. The green, red, and blue balls represent the P, O, and N atoms, respectively. (c) The Morse potential type of interaction strength between the single NO₂ molecule and the phosphorene surface with respect to the distance (defined as the height difference between the N atom and the top P atoms), as shown in (a) with the fitted curve and parameters. The inset shows the total energy change as a function of the distance from the initial ground state, as the NO₂ molecule migrates to its first nearest neighboring ground state adsorption site with the energy barriers \( \Phi_{Ba} \) and \( \Phi_{Bz} \) of 0.18 and 0.08 eV along the armchair (X direction in (a)) and zigzag (Y direction in (a)) directions, respectively. (d) Left axis: the adsorption densities
for the four target gas species (NO₂, CO, H₂S, and H₂) on phosphorene with the gas concentration fixed at 10 ppb at 300K, respectively; right axis: concentrations of CO, H₂S, and H₂ required to reach the same adsorption density of NO₂ (1.4×10^{12} \text{cm}^{-2}) at 10 ppb.

The gas adsorption was first modeled with various adsorption sites (atop site: top of phosphorus atom; bridge site: middle of the bond between two neighboring phosphorus atoms; and hollow site: the center of the phosphorus ring) and different molecular orientations (the oxygen atoms in NO₂ either pointing upwards or downwards), with the systems subsequently relaxed. The energetically favored NO₂ adsorption on phosphorene turns out to be the bridge site, with the N atom sitting above the middle of the phosphorus bond and the two O atoms pointing towards the two P atoms underneath. The binding energy \( E_b \) of NO₂ is defined as \( E_b= E_{\text{gas}}+E_P – E_{\text{gas}}+P \) where \( E_{\text{gas}} \), \( E_P \) and \( E_{\text{gas}}+P \) are the energies of a single gas molecule, pure phosphorene, and the complex system, respectively. Fig.6.1(a) presents the energetically favored molecular configuration for NO₂ adsorption. The binding energy \( E_b \) is up to 0.63 eV/molecule, which is quite large compared with those on graphene (0.21 eV/molecule) or RGO (typically 0.11~0.29 eV/molecule depending on the oxygen-containing functional groups)\(^{264}\). This can be understood from the atomic orbital bonding perspective.

The phosphorus atoms form the \( sp^3 \)-like bonding, but with one dangling bond that could interact weakly with its nearest neighbors due to the puckered honeycomb structure. In contrast to the \( sp^2 \) bonding in graphene, which has only one extra electron in the \( p_x \) orbital that forms the \( \pi \) bond responsible for NO₂ adsorption, electrons of the primitive \( s \) and \( p_x \),
$p_y$, and $p_z$ orbitals in the one dangling $sp^3$ orbital equivalent to one electron are also available for attracting NO$_2$ molecules. In other words, there are about two extra effective electrons in each phosphorus atom compared with one effective electron in each aromatic carbon atom that interact with the NO$_2$ molecule. This can also be seen by the atomic orbital-resolved density of states from Fig. 6.2, in which the $s$, $p_x$, $p_y$, and $p_z$ orbitals show a similar shape (i.e., suggesting the orbital hybridization), but the $p_z$ orbital is mostly populated by the charge associated with bands close to the Fermi level. This difference in charge density in Fig. 6.1(b) shows that the $p_z$ orbitals in phosphorus atoms surrounding the NO$_2$ molecule accept/donate electrons from/into the NO$_2$ molecule for the spin-up/spin-down state upon adsorption with net Mulliken charge transfer of 0.21e.

![Graph showing partial density of states](image-url)

**Fig. 6.2** Partial density of states (PDOS) of pristine monolayer phosphorene resolved to each atomic orbital of the valence electrons. The states are calculated using the Gaussian method with broadening of 0.075 eV.
The high binding energy of NO$_2$ molecules on phosphorene suggests good sensing performance but only on a qualitative ground. To quantitatively correlate the binding energy with BP’s superior sensitivity, statistical thermodynamics modeling was adopted to evaluate the gas-adsorption density. Fig. 6.1(c) shows the Morse potential of the gas molecule and the solid surface. Gas molecules are considered to be adsorbed on the solid surface only when $E(z)$ is negative, and the eigenstates $E_{n,z}$ can be identified by solving the Schrödinger equation. In the canonical ensemble, the gas adsorption density $n_a$ is

$$n_a = \frac{p\lambda^3}{k_BT}\prod_{l=x,y,z} q_l e^{D_l/k_BT}, \quad \lambda = \left(\frac{\hbar^2}{2\pi M k_BT}\right)^{1/2},$$  

(6.1)

where $P, \lambda, M, k_B, T,$ and $\hbar$ stand for the partial pressure, thermal wavelength and mass of the target gas species, the Boltzmann constant, the temperature, and the Planck’s constant, respectively, and $q_l = \sum_{j=0}^{n} e^{-E_{j,l}/k_BT}$ is the one-dimensional partition function. For NO$_2$ adsorption on phosphorene, the energy barrier $\Phi_{Ba}$ of 0.18 eV for its migration along the armchair direction (the inset of Fig. 6.1(c)) suggests that NO$_2$ is localized and cannot be viewed as mobile across the phosphorene surface at room temperature. As a result, the localized gas molecule can be approximated as harmonic oscillator (reasonable near the potential bottom and only the lower energy levels are of interest since they are mostly occupied) with the nondegenerate energy level $E_n = (n + 1/2)\hbar\nu$ and the frequency $\nu = \sqrt{f/M}/2\pi$, in which $f$ is the fitted force constant. Around the bottom of the migration potential, the frequencies are found to be 0.22 THz, which is typical for localized gas molecules. Along the zigzag direction, the energy barrier $\Phi_{Bz}$ of 0.08 eV implies that the gas molecules are quasi-localized around room temperature. Here, the gas molecules were treated mobile along the zigzag direction and this approximation induced the
overestimation factor that is around \( \exp(-2\Phi_{Bz}/k_BT) \) in the partition function was eliminated. With the NO\(_2\) concentration at 10 ppb and the temperature at 300 K, Eq. (6.1) reveals that the adsorption density of NO\(_2\) on phosphorene is 1.4×10\(^{12}\) cm\(^{-2}\)—this is quite high and superior to the adsorption density of NO\(_2\) (1.0×10\(^{10}\) cm\(^{-2}\)) at 10 ppb concentration on graphene at room temperature that was reported in our previous calculations\(^{264}\).

![Energetically favored adsorption models of (a) CO, (b) H\(_2\)S, and (c) H\(_2\).](image)

The adsorption densities of CO, H\(_2\)S, and H\(_2\) on BP were also modeled to understand the insensitivity of the BP towards them. Due to their much smaller binding energies (\(E_b\) is 0.23, 0.14, and 0.055 eV for CO, H\(_2\)S, and H\(_2\), respectively; also see Fig. 6.3 for adsorption sites and molecular orientations), the upper-limit adsorption density is described by Eq. (6.10)\(^{264}\). Fig 6.1d plots the resulting adsorption densities, which are 0.66×10\(^{11}\), 0.55×10\(^{8}\), and 0.31×10\(^{6}\) cm\(^{-2}\) for CO, H\(_2\)S, and H\(_2\) at 10 ppb at 300 K, respectively. Apparently, they are several orders of magnitude smaller than that of NO\(_2\). We also can compare the gas concentrations of CO, H\(_2\)S, and H\(_2\) under the same adsorption level of NO\(_2\). For example, to achieve the adsorption level of 10 ppb NO\(_2\), the required concentrations of CO, H\(_2\)S, and H\(_2\) are 0.21×10\(^3\), 0.25×10\(^6\), and 0.45×10\(^8\) ppb, respectively (Fig. 6.1(d)).
Fig. 6.4 Band structures of phosphorene upon gas adsorption. (a) The band structure of pristine phosphorene in its primitive cell. (b) Side views of the charge density distribution contour (0.05 electron/Bohr$^3$) of the LUMO and HOMO states at the Γ point (indicated by the red dots in (a)) of phosphorene. The dummy colors indicate the parities of atomic orbitals. (c) From left to right: the band structures projected into the unit cell for the single NO$_2$ molecule adsorbed in the 2×2, 3×3, and 4×4 phosphorene super-cells, respectively. (d) From left to right: the projected band structures of 4×4 phosphorene super-cells with single CO, H$_2$S, and H$_2$ molecule adsorbed, respectively. The reciprocal paths in (a), (c), and (d) are selected such that the XΓ and ΓY represent the zigzag (i.e., Y in Fig. 6.1(a)) and armchair (i.e., X in Fig. 6.1(a)) directions in the real space. The electronic structure plot shows the spatial localization of the eigenstates, indicating the relative intensity varying from low (blue) to high (red). The stray states buried in the blue
background mainly come from the local region of phosphorene with NO₂ molecule adsorption. The $k$-projection “unfolds” the bands of the supercell from the smaller Brillouin zone to the larger primitive one by decomposing the wave function into different $k$ values that can mix in the supercell, and essentially provides the straightforward information on the effect of the NO₂ molecule on the electronic properties of phosphorene upon adsorption.

The adsorption density for each individual gas species is necessary but insufficient to fully understand the distinct behaviors of BP thin film-based sensors observed in the ref²⁶⁰. For example, the NO₂ adsorption on BP thin film exhibits two distinct response modes, yet the BP thin film is still insensitive to CO, H₂S, and H₂ even at very high concentrations, and the sensitivity of BP thin film is thickness-dependent. Thus, we investigated the effect of gas adsorption on the electronic structures of the BP thin film.

The pristine single-layer phosphorene is a semiconductor with a predicted band gap of 0.92 eV (Fig. 6.4(a)), with the lowest unoccupied molecular orbital (LUMO) state and the highest occupied molecular orbital (HOMO) state at the Γ point, which is mainly formed by the $p_z$ orbitals of the phosphorus atoms (Fig. 6.4(b)). Due to the charge transfers from the $p_z$ orbitals of the phosphorus atoms to the NO₂ molecule (Fig. 6.4(b)), the LUMO and HOMO states of BP can be significantly affected by the NO₂ adsorption. For low concentrations such as <100 ppb, the NO₂ molecules affect phosphorene considerably by enhancing the hole concentration, while only slightly (or even negligibly) diminishing its carrier mobility, since the lateral distance between the adsorbed individual NO₂
molecules is quite large (>2.7 nm). Consequently, the conductance of phosphorene is enhanced linearly with a fast rate corresponding with the fast response mode in ref\textsuperscript{260}. However, this rate inevitably will be lowered by increasing NO\textsubscript{2} concentrations, because the intermolecular distance will be significantly decreased (e.g., 1.2 nm at 500 ppb) and the adsorbed NO\textsubscript{2} molecules become important scattering centers of the carriers, thereby leading to a degraded carrier mobility. To illustrate this effect, Fig. 6.4 (c) presents the $k$-projected band structures of phosphorene with NO\textsubscript{2} adsorption in several cell sizes (here the spin effect is neglected since we only focus on the states from the phosphorus atoms, and these states are not spin-polarized at room temperature). Obviously, we can see the adsorbed NO\textsubscript{2} molecules introduce a local state around the zone center, which disrupts the HOMO states into segments (this is even more severe for a smaller cell size), indicating the obstructed conducting channel for holes and thus a shorter collision time or less mobility. Also as expected, all the Fermi levels shift toward the top of the valence bands, suggesting the increase of hole concentration due to the charge transfer. Therefore, the decreased hole mobility of phosphorene upon exposure to a relatively high concentration of NO\textsubscript{2} changes the sensing response from fast mode to the slow mode.

The insensitivity of phosphorene toward CO, H\textsubscript{2}S, and H\textsubscript{2} could be attributed mainly to two factors. On one hand, in stark contrast with Fig. 6.4 (c), all electronic structures in Fig. 6.4(d) are barely altered, even using the same cell size, except for some stray states buried in the background by virtue of weak interactions between gas molecules (CO, H\textsubscript{2}S, and H\textsubscript{2}) and phosphorene, resulting in negligible changes in conductance. On the other hand, not every individual incoming gas molecule can be attracted to the phosphorene surface due to the thermal fluctuation, because the sticking coefficient/probability is
proportional to the binding energy. For CO, H₂S, and H₂ adsorption on phosphorene, the sticking coefficients at 300 K turn out to be 0.92, 0.81, and 0.59, respectively, while it increased to 1.0 for NO₂ adsorption.

6.1.2 Effect of Film Thickness on Sensitivity

In semiconductors, the electron and the hole concentrations can be obtained as follows:

\[
n_e = 2 \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^\frac{3}{2} \exp\left( \frac{E_F - E_C}{k_B T} \right), \quad n_h = 2 \left( \frac{m_h k_B T}{2\pi \hbar^2} \right)^\frac{3}{2} \exp\left( \frac{E_V - E_F}{k_B T} \right),
\]

(6.2)
in which \( m_e (m_h) \) is electron (hole) mass, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \hbar \) is the Planck’s constant, \( E_F \) is the Fermi level, \( E_C \) (\( E_V \)) is the conduction (valence) band edge energy. From Eq. (6.2), we could derive the following expressions straightforwardly,

\[
n_e n_h = 4 \left( \frac{k_B T}{2\pi \hbar^2} \right)^3 (m_e m_h)^\frac{3}{2} \exp\left( -\frac{E_g}{k_B T} \right)
\]

(6.3)

and

\[
\frac{n_e}{n_h} = \left( \frac{m_e}{m_h} \right)^\frac{3}{2} \exp \left[ \frac{2(E_F - (E_C + E_V))}{k_B T} \right] = \left( \frac{m_e}{m_h} \right)^\frac{3}{2} \exp \left[ \frac{2(E_F - E_{F_i})}{k_B T} \right] \approx \exp \left[ \frac{2(E_F - E_{F_i})}{k_B T} \right].
\]

(6.4)

Here, \( E_g = E_C - E_V \) is the band gap, and \( E_{F_i} \) is the intrinsic Fermi level. In Eq. (6.4), the prefactor \( (m_e/m_h)^\frac{3}{2} \) can be neglected since the difference between the hole and electron effective masses are usually small (within one order of magnitude), while the accurate values needs the parabolic fittings of the states located at the conduction band minimum and the valence band maximum in the electronic structure.

The conductivity of the semiconductor is calculated as
\[ \sigma = e(n_e\mu_e + n_h\mu_h) \]  

where \( e \) is the elementary charge and \( \mu_e (\mu_h) \) is the electron (hole) mobility. We define the conductivity ratio from the electron and hole part as

\[ R = \frac{en_e\mu_e}{en_h\mu_h} \quad \text{or} \quad \frac{en_h\mu_h}{en_e\mu_e} \approx \frac{n_e}{n_h} \quad \text{or} \quad \frac{n_h}{n_e} = \exp \left[ \frac{2|E_F - E_{Fi}|}{k_B T} \right] \geq 1 \]  

(6.6)

for \( n \)-type or \( p \)-type semiconductors. Note that in Eq. (6.6), we have assumed \( \mu_e \approx \mu_h \) for simplicity and the difference between them is mostly less than one order of magnitude. For specific materials, this difference can be considered for better accuracy. After the following algebra,

\[ R = \frac{n_e}{n_h} \rightarrow n_h = \frac{n_e}{R} \quad \text{and thus} \quad n_e n_h = n_e \left( \frac{n_e}{R} \right) = \frac{n^2_e}{R} \rightarrow n_e = (n_e n_h R)^{\frac{1}{2}}, \]

we obtain,

\[ n_e = 2 \left( \frac{k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} (m_e m_h)^{\frac{3}{2}} \left\{ \exp \left[ -\frac{E_g - 2(E_{F_n} - E_{Fi})}{k_B T} \right] \right\}^{\frac{1}{2}} \]  

(6.7)

and

\[ n_h = 2 \left( \frac{k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} (m_e m_h)^{\frac{3}{2}} \left\{ \exp \left[ -\frac{E_g - 2(E_{Fi} - E_{F_h})}{k_B T} \right] \right\}^{\frac{1}{2}} \]  

(6.8)

for the \( n \)-type and \( p \)-type semiconductors with Fermi level \( E_{F_n} \) and \( E_{F_h} \), respectively.

In electrical conductance based gas sensors, the sensitivity for \( n \)- or \( p \)-type semiconductors is defined as

\[ S = \frac{\sigma - \sigma_0}{\sigma_0} = \frac{e(n_e\mu_e - n_e0\mu_{e0})}{e(n_e0\mu_{e0} + n_h0\mu_{h0})} \quad \text{or} \quad \frac{e(n_h\mu_h - n_h0\mu_{h0})}{e(n_e0\mu_{e0} + n_h0\mu_{h0})} \]  

(6.9)

where \( \sigma_0 \) and \( \sigma \) are the conductance before and after the target gas adsorption. Note that the sign of the sensitivity in Eq. (6.9) depends both on the gases and semiconductors. For \( n \)-type semiconductors, the sign is positive (negative) for reducing (oxidizing) gases and
vice versa for the p-type semiconductors. It is For a low gas concentration, the gas adsorption density is small and the gas distribution is so sparse that the gas adsorption induced scattering effect on the carrier mobility can be neglected (i.e., $\mu_e \approx \mu_{e0}$ and $\mu_h \approx \mu_{h0}$). Therefore, Eq. (6.9) is then reduced to

$$S = \frac{\Delta n_e}{n_{e0} + n_{h0}} \text{ or } \frac{\Delta n_h}{n_{e0} + n_{h0}}$$

(6.10).

For n-type or p-type semiconductors, $n_{e0} \gg n_{h0}$ or $n_{h0} \gg n_{e0}$ holds and thus,

$$S = \frac{\Delta n_e}{n_{e0}} \text{ or } \frac{\Delta n_h}{n_{h0}}$$

$$= \frac{\Delta Q / t}{n_{e0}} \text{ or } \frac{\Delta Q / t}{n_{h0}}$$

$$= \left\{ \frac{\Delta Q}{r} \left[ \exp \left( \frac{E_g - 2(E_{Fn} - E_{Fi})}{k_B T} \right) \right] \right\} \text{ or } \left\{ \frac{\Delta Q}{r} \left[ \exp \left( \frac{E_g - 2(E_{Fp} - E_{Fi})}{k_B T} \right) \right] \right\}$$

(6.11).

In a compact form, Eq. (6.11) can reformulated as

$$S = \left\{ \frac{\Delta Q}{r} \left[ \exp \left( \frac{E_g - 2|E_{Fi} - E_{Fp}|}{k_B T} \right) \right] \right\}$$

$$= \frac{\Delta Q}{2 \left( \frac{k_B T}{2 \pi m^*} \right)^{3/2} (m_e m_h)^{3/4}}$$

(6.12).

Here, $\Delta Q$ is the charge transfer per planar unit area in a 2D film that can be determined with the knowledge of gas adsorption density, and $t$ is the film thickness. Eq. (6.12) suggests that sensitivity is highest in the intrinsic semiconductor than its n-type or p-type counterpart. This is consistent with experimental observations that the sensitivity increases (decreases) after applying a positive (negative) gate voltage$^{260}$, since for the p-type semiconductor the positive (negative) gate voltage will shift the Fermi level $E_{Fp}$ upwards (downwards) and thus decrease (increase) the energy spacing $(E_{Fi} - E_{Fp})$ as illustrated in Fig. 6.5.
Since the sensitivity is dependent on the thickness of the BP thin film, we define the sensitivity ratio as

$$
\frac{s(t)}{s(t_0)} = \frac{\Delta Q(t)}{t_0} \left\{ \exp \left( \frac{E_g(t) - 2|E_F(t) - E_{Fi}(t)|}{k_BT} \right) \right\}^{1/2} = \frac{t_0}{t} \frac{n_a(t)\Delta q(t)}{n_a(t_0)\Delta q(t_0)} \exp \left[ \frac{E_g(t) - E_g(t_0) + 2|E_F(t_0) - E_{Fi}(t_0)| - 2|E_F(t) - E_{Fi}(t)|}{2k_BT} \right].
$$

(6.13)

Here $\Delta q$ is the charge transfer of the individual gas molecules. As the band gap of the BP film decreases when the film thickness increases, especially in the thin film regime from monolayer up to ~10nm thick (the bandgap then barely changes and reaches a constant at the bulk value), we divide the BP film into the thin film (0.5-10 nm) and thick film (>10 nm) regimes. In the thin film regime, the carrier mobility of BP is also slightly thickness-dependent due to the scattering effect from the substrate impurities, and Eq. (6.13) is accordingly modified to take the mobility effect into account as

$$
\frac{s(t)}{s(t_0)} = \frac{t_0}{t} \frac{n_a(t)\Delta q(t)}{n_a(t_0)\Delta q(t_0)} \mu(t) \exp \left[ \frac{E_g(t) - E_g(t_0) + 2|E_F(t_0) - E_{Fi}(t_0)| - 2|E_F(t) - E_{Fi}(t)|}{2k_BT} \right].
$$

(6.14)
Fig. 6.6 Schematic of the effective thickness variation with respect to the actual film thickness. The colored bar indicate the actual film thickness $t$.

For the thick film, as the band gap barely changes, which also holds for the binding energy (and consequently for the charge transfer, adsorption density and the Fermi level), Eq. (6.14) is reduced to

$$\frac{s(t)}{s(t_0)} = \frac{t_0 \mu(t)}{t \mu(t_0)}. \tag{6.15}$$

Note that the thickness $t$ in Eq. (6.15) should be replaced by the effective thickness, because the charge transfer upon the gas adsorption is not uniformly distributed in the entire film due to the layered 2D nature (the out-of-plane conductivity is much smaller than the in-plane one); it is accumulated mostly at the surface region with a certain penetration depth that would vary with respect to the film thickness $t$, as illustrated in Fig. 6.6. Here, we empirically take this effective thickness as

$$t_{eff} = \frac{(1+a)\beta \lambda}{1+a \beta \lambda}, t \geq \beta \lambda \tag{6.16}$$
where $\lambda(=2.9\text{nm}^{92})$ is the Thomas-Fermi charge screening length, $\alpha$ and $\beta$ are constants that need to be obtained from experimental data. Hence, the sensitivity for thick film is

$$s(t) = \frac{1+\alpha \frac{\mu(t)}{\mu(t_0)}}{1+\alpha \frac{\mu(t_0)}{\mu(t_0)}}$$

(6.17)

To predict the sensitivity, we first start with the binding energy $E_b$ variation of different layers of phospherene. Due to the severe underestimation of band gaps from DFT calculations, we fit the calculated binding energies/band gap values and then make the extrapolation with respect to the faithful energy gaps$^{92}$. We can see from Fig. 6.7(a) that as expected $E_b$ increases from the monolayer (0.18eV) all the way up to and saturates at the bulk limit (0.83eV), since the BP films with a smaller gap (i.e., larger carrier concentration) could enable more charge transfer into the gas molecules. Assuming the energy barriers vary linearly with respect to the binding energy, the corresponding predicted NO$_2$ adsorption density by Eq. (6.1) is lowest for the monolayer ($\sim 10^7\text{ cm}^{-2}$) and keeps increasing to the bulk limit ($\sim 10^{16}\text{ cm}^{-2}$).

Next, we adopt the Eq. (6.14) and (6.17) to predict the sensitivity. Note that $\Delta Q$ is also linearly proportional to the gas adsorption density $n_a$. Here, we assume that $\Delta q$ also is linearly proportional to $E_b$ and uses the extrapolated Fermi energy spacings$^{266}$. In addition, we have to judiciously select the values of $\alpha$ and $\beta$ that have distinctive physical meanings. The penetration depth of surface charge is dependent on the film thickness: for very thin film, it is equal to the actual film thickness $t$; for thick films, although it is always smaller than $t$, it begins to increase with the increasing film thickness $t$. Thus, there exists a critical thickness $t_c$ that separates these two scenarios.
Here, we choose $t_c = \beta \lambda = 10 nm$. On one hand, the gas adsorption induced carrier concentration at $t_c$ with respect to the surface concentration is reduced to $\exp(-t_c/\lambda) = 3.2\%$ and thus the adsorbed gas molecules would affect the carrier concentration within the entire film with $t < t_c$. On the other hand, the carrier mobility extracted from the field effect measurements show that the carrier mobility increases from the monolayer to the thin film.
Fig. 6.7 Dependence of Film thickness on sensitivity. (a) Left axis: relative binding energy with respect to the monolayer as a function of the band gap. The black dots are the theoretically predicted values; the red dots are the linearly extrapolated values with the layer number of phosphorene labeled; the blue dots are the extension of the linear fitting into the region of underestimated band gaps; Right axis: the gas molecule adsorption density in 10 ppb NO$_2$ at 300K. (b) Sensitivity obtained from Eqs. (6.14) and (6.17) for 500 ppb NO$_2$ concentration, together with those scaled to the concentrations of 100 and 20 ppb using the sensitivity ratio from Fig. 2 in the ref$^{260}$, respectively. The hollow symbols indicate the case when the effect of mobility degradation is not considered. The inset is the zoomed-view of the sensitivity for the film thickness from 30nm to the bulk. Note that the thickness for the monolayer phosphine is 0.5nm.

with $t = 10nm$ and then slightly decreases as the film thickness $t$ increases. The physical meaning of $\alpha$ is that $t_{eff}$ will increase with a decreasing rate upon the application of source-drain voltage which pushes the carriers to penetrate through the film. The value of $\alpha$ (=5) can be obtained by the ratio of sensitivity experimentally measured at 40 nm and 200 nm BP thin film and the ratio of the mobility at different film thickness.

Fig. 6.7(b) shows the predicted sensitivity with respect to the film thickness (from monolayer to bulk) for the NO$_2$ concentrations of 500, 100 and 20 ppb, respectively. It can be seen that the sensitivity first increases and then decreases as the film thickness increases, and the highest sensitivity should be realized experimentally at the film thickness from several to $10^+$ nm. This is even true when the mobility degradation is not
considered. Physically, this arises from the fact that semiconductors with a larger band gap have a poor ability to attract gas molecules due to their lower carrier concentrations, while the conductivity variation is less likely for semiconductors with a smaller band gap due to their higher carrier concentrations. Therefore, there would be an optimum band gap range for the high sensitivity by balancing these two effects. Note that the predicted sensitivities in the thin film regime will deviate from the faithful values to some extent due to the underestimation/overestimation in evaluating the gas adsorption density; however, the predicted trend of sensitivity is qualitatively reliable.

6.2 Illumination on the Effect of Oxidation on BP Sensing Behavior through Experiments and DFT Modeling

Despite the super sensitivity of BP thin films, it can be oxidized in ambient air. Thus, it is important to investigate how surface oxidation will affect sensitivity. In this section, we fabricated the BP FET sensor and characterized its sensor performance.

Fig. 6.8 (a) shows a schematic of the BP FET device and the circuit for electrical and sensing measurements. The nanoscale FET sensor was fabricated by transferring the mechanically exfoliated BP thin films from commercial bulk BP onto the SiO$_2$/Si substrate patterned with the Au electrodes. Then, the sensor was annealed in the Ar atmosphere at 200 °C for 1 hour to improve the electrical contacts between the BP thin film and the gold electrodes. The SEM image in Fig. 6.8(b) clearly shows that the BP thin film bridges the gap of the gold fingers and works as the conducting channel in the FET sensor. To determine the thickness of the BP film, AFM was performed, as shown in Fig. 6.8(c)-(d), and the height profiles indicate that the film thickness is ~35nm, suggesting a
Fig. 6.8 (a) Schematic of the BP-based FET device; (b) SEM image of the BP thin film connecting the Au electrodes; the scale bar is 3µm with the length (L=2.25 µm) and width (W=3.5 µm) indicated; (c) AFM image of the BP thin film as shown in (b): the white lines (L₁, L₂, L₃) are the regions where the height measurements are performed; (d) the height profiles of the BP thin film for the regions shown in (c) and the film thickness is estimated to be 35 nm.

layer number of ~66. Note that such a thick film would electronically behave more like the bulk BP due to the similar band gap; however, the sensor performance would be different, as discussed in Section 6.1.2.
Fig. 6.9 (a) The band alignment between the Au electrode and BP before and after contact, where $\phi_m$ ($\phi_s$) is the metal (semiconductor) workfunction, $\chi$ is the electron affinity in the semiconductor, $E_C$($E_V$) is the edge conduction (valence) band, $E_F$($E_{Fi}$) is the (intrinsic) Fermi level, $\phi_{Bh}$ and $\phi_{Be}$ are the Schottky barriers for the holes and electrons, respectively; (b) the dynamic response of the as-fabricated BP sensor in terms of the source-drain current ($I_{DS}$) change with $V_{DS} = 5$ mV before and after exposure to NO$_2$ gases diluted in air with respect to gas concentrations ranging from 5 to 1,500 ppb. The color-coded regions stand for the duration (10 min) of gas exposure and the inset is the I-V curve.

Prior to presenting the sensing performance analysis, we first discuss the contact resistance between the BP thin film and the gold electrodes. In principle, this contact resistance is composed of two parts: the physical contact induced resistance and the Schottky barrier induced resistance. While the former can usually be minimized by the thermal annealing treatment, the latter is inherent to the workfunction difference between the metal and the semiconductor. Fig. 6.9 (a) shows the schematics of band alignment between the Au electrode and the BP thin film. Before the direct contact, the Fermi level of BP lies above that of Au, since the workfunction of Au is 5.1 eV, larger than 4.5 eV for BP. Consequently, electrons will be transferred from BP into Au at the interface upon contact and the Fermi level $E_F$ will move away from (towards) the edge conduction (valence) band $E_C$ ($E_V$) due to the decrease (increase) of the electron (hole) concentration, causing the band bending upwards and negative (positive) Schottky barrier $\phi_{Bh}$ ($\phi_{Be}$) for the hole (electron) transport. Since BP is a p-type semiconductor (the Fermi level $E_F$ lies below the intrinsic one $E_{Fi}$), the negative Schottky barrier $\phi_{Bh}$ for hole indicates that
Ohmic contact between Au and BP can be realized. This is verified by the linear I-V characteristic as shown in the inset of Fig. 6.9(b), suggesting an efficient injection channel for holes at the interface that minimizes the interface’s influence on the intrinsic sensing properties of the as-fabricated gas sensor.

The dynamic-sensing response of the BP thin film-based FET sensor toward NO$_2$ in air at room temperature was then monitored by recording the source-drain current ($I_{DS}$) change at a constant source-drain bias $V_{DS}=5$ mV before and after exposure to NO$_2$. We can see from Fig. 6.9(b) that the current change increases as the NO$_2$ concentration varies from 5 to 1,500 ppb, which is expected, since the higher concentration led to more gas adsorption on the surface of the BP thin film. Since NO$_2$ is an oxidizing gas and BP is a p-type semiconductor (i.e., the hole is the major carrier), the surface adsorbed NO$_2$ molecules will withdraw electrons from the BP thin film and effectively increase the hole concentration, thereby increasing the electrical conductivity or the current. However, we observed an anomalous behavior: the current experienced an initial decrease for all gas concentrations studied here. Close examination of Fig. 6.9(b) shows that the dynamic sensing response can be characterized in two scenarios. At low gas concentrations (<20 ppb), the current keeps decreasing during gas exposure (10 min); at higher gas concentrations (from 30 to 1,500 ppb), the current first decreases and then increases over the gas exposure. The critical gas concentration that separates the two scenarios for the sample studied here is ~40 ppb.

The unusual source-drain current behavior is strongly indicative of some new type of surface interactions in the sensor. Considering that BP can oxidize in air with the
Fig. 6.10 (a) Room temperature dynamic response to 500 ppb NO$_2$ for the same BP thin film FET sensor before (pristine in dry air) and after oxidization (in wet air) with the source-drain voltage $V_{DS}$ fixed at 4 mV and 7 mV, respectively. The inset is the zoomed-in view of the circled region and the short olive dash lines are used to guide the observation. (b) The most energetically preferred NO$_2$ adsorption on pure phosphorene
and different adsorption situations of NO$_2$ on surface oxidized phosphorene. The binding energies are relative to those for the adsorption on pristine phosphorene.

presence of water molecules, the initial current decrease could be ascribed to the potential interaction between the NO$_2$ molecules and the oxidized region since the sensor investigated in Fig. 6.9(b) was kept under the ambient condition. To validate this hypothesis, a control experiment was conducted by comparing the current behavior for the same sample under the following scenarios: first, the exfoliated BP thin film was kept in dry air after the thermal annealing and the sensor performance was recorded; then, the sensor was stored under the ambient condition for 2 days to realize the oxidation and the gas sensing performance was tested again. Fig. 6.10(a) shows the sensing results in 500 ppb NO$_2$. At first glance, the current increase is more pronounced in the oxidized BP thin film than that in the pristine counterpart. The current is enhanced from 210 nA for the pristine BP to 310 nA for the oxidized BP thin film right at the end of gas exposure with the similar initial current before the gas exposure. This suggests that the surface oxidation is beneficial for improving the gas sensitivity. Moreover, as shown in the inset of Fig. 6.10(a), the zoomed-in view of the dynamic sensing response clearly shows a current dip at the initial stage of the gas exposure for the oxidized BP thin film in contrast to the all the way increase for the pristine BP thin film, revealing that this initial current decrease uniquely arises from the surface oxidation. To thoroughly understand such experimental observations, DFT calculations were then carried out with respect to various surface adsorptions and their strength with and without the surface oxidation of phosphorene (for the most energetically favored atomic oxygen configuration). We can see from Fig. 6.10(b) that the NO$_2$ molecules are preferrably attracted to and dissociated by the surface
atomic oxygen atoms, resulting in the formation of P-O and the absorption of NO in the nearby region. Despite the fact that the adsorbed NO molecule will draw electrons from the underlying phosphorene and lead to the increase of hole concentration (and thus, current increase), the formed P-O bond of the oxygen atom from the dissociated NO\textsubscript{2} molecule will distort the local puckered structure further, thereby degrading the carrier mobility as well as the energy band gap increase (and thus, current decrease). Therefore, the overall effect is that the current decreases upon the dissociation of NO\textsubscript{2} since the latter effect is more dominant. Note that NO\textsubscript{2} adsorption is not energetically favored near the oxidized region since the relative binding energy (-0.21 eV) is negative compared with the adsorption on pure phosphorene, also suggesting that NO\textsubscript{2} will likely be dissociated by the oxidized region.
Fig. 6.11 (a) Raman spectrum of the oxidized BP thin film on Si substrate, the inset is the zoomed-in view of the wave number range from 540 to 900 cm\(^{-1}\); (b) time evolution of the Raman spectra of the BP thin film from freshly exfoliated sample up to 18 days after preparation; (c) and (d) are the predicted Raman spectra of pristine and surface oxidized monolayer phosphorene, respectively. The spectra are convoluted with Gaussian function with broadening of 7.5 cm\(^{-1}\). The inset shows the structure for the Raman modes calculation which is most energetically favored (and is also used for gas adsorption, as shown in Fig. 6.10(b)).

(leading to the current decrease) and the adsorption in the region far away (leading to the current increase) will only occur when the dissociation is completed.
To further support the above analysis that the surface oxidation is responsible for the experimental sensing observations, both the experimental Raman measurement and the theoretical prediction of Raman modes were performed. Fig. 6.11(a) shows the experimentally measured Raman spectra for the oxidized BP on the Si substrate. We can identify three Raman peaks located at around 360, 439, and 465 cm\(^{-1}\), corresponding with the \(A_{2g}\), \(B_{2g}\), and \(A_{1g}\) modes of the pristine BP, in good agreement with previous observations\(^{267,268}\). However, several new peaks (818, 830, and 867 cm\(^{-1}\)) also appear in the region from 800 to 900 cm\(^{-1}\) as seen from the inset in Fig. 6.14(a) and these peaks are not from the Si substrate. Moreover, these peaks also grow with time (Fig. 6.11(b)). The predicted Raman spectrum of pure monolayer phosphorene, shown in Fig. 6.11(c), also shows three peaks, with the peak wavenumber 373, 445, and 478 cm\(^{-1}\) close to the experimental values (with only slight overestimation no more than 15 cm\(^{-1}\)), suggesting the success of theoretical prediction. After the oxidation, four new peaks appear for both strained and relaxed structures (depending on the local environment) with the wavenumber centered around 584, 691, 821(853), 891(904) cm\(^{-1}\). Considering the slight wavenumber overestimation, the predicted peaks at 821, 853, 891 and 904 cm\(^{-1}\) fall well within the experimentally observed frequency region. Note that the predicted peaks at 584 and 691 cm\(^{-1}\) are more likely to be buried in the Si background. Therefore, it can be concluded that the unusual sensing behavior observed in Fig. 6.9(b) indeed results from the surface oxidation of BP thin films.

As shown in Fig. 6.9(b), the current increase is not proportional to the gas concentration and the rate of increase decreases as the gas concentration increases. This effect is also observed in other sensing tests reported in the literature. In principle, this is mainly due to
two reason. First, not every individual incoming gas molecule will be absorbed onto the surface of the BP thin film,
**Graph (c):**

- Black line: In Air
- Red line: 100 ppb
- Blue line: 500 ppb
- Green line: 1000 ppb
- Purple line: 1500 ppb

Graph shows the relationship between $I_{DS}$ (nA) and $V_{BG}$ (V).

**Graph (d):**

- Equation: $g_m = \frac{dI_{DS}}{dV_{BG}}$
- Equation: \[ \mu_{FE} = \frac{L}{W CV_{DS}} \]

Graph shows the relationship between $g_m$ (nS) and $NO_2$ (ppb).
Fig. 6.12 (a)-(c) Room temperature transfer characteristic for the FET with an applied bias voltage $V_{DS}=5\text{mV}$ and a back gate voltage $V_{BG}$ swept from -35 V to +35 V without and with exposure to NO$_2$ gases in the concentration range from 5 to 1,500 ppb, as shown in Fig. 6.12(b); (d) the extracted transconductance and carrier mobility from FET curves in (a)-(c).

especially for the high gas concentrations since the binding energy of gas molecules will decrease for higher adsorption densities and multilayer adsorption will occur for very high gas concentrations; second, the carrier mobility would be degraded for denser adsorption because the adsorbed gas molecules become significant scattering centers that cannot be neglected. To illustrate this effect, the mobility is extracted from Eq. (2.18) with capacitance ($C=1.73\times10^{-4}\text{Fm}^{-2}$) calculated from the parallel-plate model based on the FET measurements. Fig. 6.12(a)-(c) show the transfer characteristics of the FET sensor both in air and in NO$_2$ with different concentrations corresponding with the sensing test in Fig. 6.9(b). We can see that the as-fabricated sensor shows p-type semiconducting behavior. The extracted field mobilities in Fig. 6.12(d) reveal that the mobility degradation occurs when the gas concentration is higher than 20 ppb. For the bare sensor in air, the hole mobility is 160 cm$^2$V$^{-1}$s$^{-1}$, smaller than the reported value of 286 cm$^2$V$^{-1}$s$^{-1}$ in vacuum due to the potential scattering from air (mostly from the water molecules) and the two terminal measurements that likely lead to underestimation. Also note that the mobility degradation rate decreases for higher gas concentrations, because the adsorbed gas molecules would work as the top dielectric medium (despite low $\kappa$) to screen the Coulombic scattering of charge impurities trapped at the interface between the substrate and the BP thin film, as analyzed in Section 2.3.
6.3 Summary

In this chapter, gas sensing properties are analyzed both theoretically and experimentally on BP thin film-based FET sensors. First-principles calculations show that the binding energy of NO\textsubscript{2} varies from 0.18 eV/molecule on bulk BP to 0.83 eV/molecule on monolayer phosphorene, leading to a NO\textsubscript{2} adsorption density from \( \sim 10^7 \text{ cm}^{-2} \) to \( \sim 10^{16} \text{ cm}^{-2} \), even for 10 ppb NO\textsubscript{2} at 300 K. The predicted sensitivity further suggests that the highest sensitivity can be realized for film thicknesses from several to 10+ nm. Moreover, unlike the pristine BP thin film-based sensor, an anomalous behavior is observed for surface oxidized BP sensors: at low gas concentrations (<20 ppb), the current keeps decreasing during gas exposure (10 min) while at higher concentrations (from 30 to 1,500 ppb), the current first decreases and then increases during the gas exposure. DFT calculations show that the NO\textsubscript{2} molecules prefer to be attracted to and dissociated by the surface atomic oxygen, resulting in the formation of P-O and the adsorption of NO in its vicinity. Although the adsorbed NO molecule draws electrons from the underlying phosphorene, which leads to the increase in the hole concentration (corresponding with current increase), the formed P-O bond with the oxygen atom from the dissociated NO\textsubscript{2} molecule will distort the local puckered structure further, resulting in the carrier mobility degradation as well as the energy band gap increase (corresponding with current decrease). The overall effect is that the current decreases upon the dissociation of NO\textsubscript{2} since the latter effect is dominant. However, the current will start to increase when the dissociation is completed for sufficiently long gas exposure or high gas concentrations. The superior sensitivity makes BP outstanding in gas sensor applications; however, its stability needs to be considered for practical uses.
CHAPTER 7 CONCLUSIONS AND OUTLOOK

7.1 Conclusions

DFT calculations show that there are three infrared-active vibration modes ($B_{1u}$, $B_{2u}$, and $B_{3u}$) and six Raman-active modes ($B_{1g}$, $B_{2g}$, $2B_{3g}$, and $2A_g$) for intrinsic GMO. The frequencies of these infrared modes depend on both the local structural deformations resulting from the embedding of GMO in a graphene matrix and the interactions between the adjacent GMO layers. In addition, the band gap of GMO can be tuned over a large range (0-1.35 eV) for accessible strains. The electron and hole transport occurs predominantly along the zigzag and armchair directions (armchair for both) when GMO is a direct- (indirect-) band gap semiconductor. Moreover, the predicted room temperature thermal conductivity (>3,000 Wm$^{-1}$K$^{-1}$) of GMO is 80% that of graphene along the armchair direction for large sample lateral sizes (>5 µm). And the lattice thermal conductivity along the armchair direction in GMO is about five times higher than that along the zigzag direction. Heat is predominantly carried by longitudinal phonons along the armchair direction, while the contribution from the transverse acoustic phonon mode is prevalent along the zigzag direction. While the theoretically predicted IR spectra offers further insights for its structure identification and layer number characterization, the predicted tunable band gap and high thermal conductivity make GMO a promising candidate for next generation of nanoelectronics applications.

Epoxy pair chain essentially produces finite spin moment for both the AFM and the FM coupling between the ribbon edges of the ZGNR, while oxidized ZGNRs with two single
epoxy chains and pure ZGNRs show the trivial moment for the AFM coupling. The total spin moment has a weak dependence on the position of single epoxy and epoxy pair chains inside the ZGNR and on the width of the ZGNR. In addition, the ZGNR oxidized by one epoxy pair chain transitions from a half-metal to a semiconductor by tuning the Fermi level when the chain shifts inwards from the ribbon edge, suggesting the potential for designing graphene-based spintronics by introducing epoxy pair chains.

By testing CO, NO, NH$_3$ and NO$_2$ adsorbed on graphene and RGO, our statistical thermodynamics models show that the adsorption density and coverage can be effectively estimated by the binding energy of a gas molecule with high accuracy. The results help to assess the gas sensing performance without fitting the Morse potential or solving the Schrödinger equation. The models on the gas adsorption density and on the sensitivity for semiconductors offer quantitative understanding of nanoscale gas sensors and provide guidance in sensor design. The van der Pauw and Hall measurements on the TRGO thin films-based gas sensors further suggest that the conductance change of the thin film after exposure to the NO$_2$ molecules largely arises from the carrier concentration rather than the carrier mobility. Moreover, the sensitivity of graphene-based gas sensors can be enhanced by coating these materials with nanocrystalline particles.

For the BP thin film-based gas sensors, the theoretically predicted binding energy of NO$_2$ molecules on monolayer phosphorene to bulk BP varies from 0.18 to 0.83 eV/molecule, leading to a NO$_2$ adsorption density from $\sim 10^7$ cm$^{-2}$ to $\sim 10^{16}$ cm$^{-2}$, even for 10 ppb NO$_2$ at 300 K. Our sensitivity modeling suggests that the highest sensitivity can be realized for
a film thickness from several to 10+ nm with the carrier mobility degradation considered due to the trapped impurity charges at the interface between the BP thin film and the substrate. However, without considering the effect of mobility degradation, our modeling indicates that the optimum film thickness is around 4 nm, corresponding with BP with eight layers and a band gap of ~0.6 eV. Our DFT calculations further show that the surface atomic oxygen atoms in the oxidized BP sensors will attract and dissociate NO₂ molecules, resulting in the formation of P-O and the adsorption of NO in the nearby region. The former will distort the local puckered structure further and degrade the carrier mobility as well as the energy band gap increases, while the latter will increase the hole concentration. However, the former effect is dominant and the overall current decreases upon the dissociation of NO₂. Nevertheless, the current will start to increase when the dissociation is completed and saturated for sufficiently long exposure or high gas concentrations.

7.2 Outlook

Despite the predicted tunable bandgap in a wide range and a high thermal conductivity that make GMO promising in future electronics applications, two major concerns still need to be addressed. First, our predicted bandgaps from conventional DFT calculations are certainly underestimated since the effect of interactions between electrons is not considered. More faithful values of the band gaps can be obtained by adopting the hybrid exchange-correlation functional like Heyd-Scuseria-Ernzerhof or Green function with the screened interaction (i.e., the GW approximation). Second, although IR spectra have been
simulated to help identify the formation of GMO, it is still desirable to offer theoretical insights into the thermal reduction dynamics of GO and how the epoxy pair domains evolve at a large scale. Currently, GMO can only be experimentally produced in small domains with the graphene/TRGO matrix under thermal reduction in vacuum at a high temperature. And GMO domains are only found in thick GO films rather than the monolayer or few-layer GO. Moreover, the temperature of >600 °C is high enough to remove most of the oxygen-containing functional groups in GO, but it is unclear why the formation of GMO is energetically preferred over the release of CO/CO₂ molecules by removing the functional groups.

To answer these questions, the following future studies are suggested: (1) using the NEB method to calculate the migration barriers for epoxy groups along the underlying carbon skeleton in monolayer GO and search for the most energetically favored path to form the single epoxy pair by manually setting different paths, and furthermore the variation of the barrier height with respect to the GMO domain size; (2) following the procedure in step (1) by replacing the monolayer GO with the multilayer GO and compare the resulting energy barrier for the formation of GMO domains; (3) varying the interlayer distance of GO to mimic the pressure during the thermal reduction and observe how the energy barrier changes. Note that the above suggested calculations must be conducted using a code of molecular dynamics embedded with an NEB algorithm in which temperature effect also can be considered. Moreover, much larger system sizes can be simulated with more affordable computation efforts than the DFT codes.
For the gas adsorption, we considered both the mobile and (quasi-)localized adsorption but our model currently can be used only to quantitatively characterize the adsorption density for the monolayer gas adsorption. Experimentally, it is obvious that the multilayer adsorption can occur beyond a critical target gas concentration. Consequently, several parameters need to be corrected in the future modeling of multilayer adsorption. First, the partial target gas pressure becomes larger and must be determined by establishing the thermodynamics modeling. Second, the binding energies of gas molecules in different layers vary and the binding energy becomes lower for gas molecules further away from the adsorption surface; third, the physical meaning of gas adsorption density might be inappropriate for the multilayer adsorption; instead, the concept of adsorption coverage can be used by employing the Brunauer–Emmett–Teller equations with the gas saturation pressure from the standard tables. Even for the monolayer adsorption, the binding energies of gas molecules are also functions of the adsorption density and the binding energy increases as the gas concentration decreases, suggesting that the characterization of gas adsorption density is underestimated, especially for very low gas concentrations and more accurate density can be obtained theoretically by calculating the binding energy in sufficiently large supercells. Moreover, our proposed model to predict the sensitivity is applicable to semiconducting materials irrespective of their dimensionality. However, future studies should be conducted so that the optimum semiconductor can be identified for gas sensing applications, even for the same type of structures like 2D transition metal dichalcogenides by varying the composition.
Although we have developed models of gas adsorption density and sensitivity for semiconducting materials, they are still inadequate to characterize the performance of a real gas sensor. Practically, it is intriguing to establish the modeling to characterize the gas adsorption dynamics, namely, the gas adsorption rate and the gas desorption rate. This is significant since both the detection limit and response time/recovery rate are critical in evaluating the performance of a real sensor. And a good sensor should achieve both instead of sacrificing one to achieve the other. Here we propose the following approaches to this end for future studies. First, the adsorption rate is approximated by the classic theory so that it is equal to the gas incoming rate that depends only on the temperature and the mass of the gas molecule, while the desorption rate is dependent on both the temperature and the gas binding energy. Second, the conductance can be predicted by nonequilibrium Green function with respect to the distance between the gas molecule and the adsorption surface. Third, the adsorption/desorption time can be finally determined by adsorption/desorption rate and the conductance change.

Practically, hybrid structures composed of 2D thin film/1D nanowires and 0D nanoparticles can be used to enhance the sensitivity toward specific gas species, in which the underlying the 2D/1D materials work as the conducting channel while the 0D nanoparticles work as the primary sites to attract gas molecules. Our current model treats the two parts separately, i.e., neglecting the effect of nanoparticle on the electronic properties of the underlying 2D/1D materials. In principle, charge transfer occurs due to the mismatch between the 2D/1D materials and the 0D nanoparticles, leading to the band bending at the interface. However, it is unclear whether the potential synergetic effect
exists in the gas sensing or not. As our sensitivity model for semiconducting materials suggests there is an optimum range of bandgap for the gas sensitivity and neither too large nor too small of a bandgap is beneficial for the gas sensitivity. Thus, it is necessary to develop models by considering the effect of the nanoparticles on the effective bandgap (or carrier concentration) of the underlying 2D/1D materials to demonstrate such a synergetic effect. As the conductivity of semiconductors is the product of the carrier concentration and the carrier mobility, our van der Pauw measurements on TRGO thin films suggest that the carrier concentration change is dominant. Further studies on the effect of carrier concentration and mobility change after the nanoparticle decoration on the 2D/1D materials surface are warranted to understand the synergetic effect.

For the BP thin film-based gas sensor, it can be oxidized in air with the aid of water molecules. Despite enhanced sensitivity due to the oxidized region, BP thin films cannot sustain in air with humidity for long time, and fully oxidized BP thin films might not be suitable for gas sensing applications. Experimentally, it is still essential to monitor the dependence of gas sensing properties of the BP thin film on ambient conditions with respect to time. Moreover, our model in interpreting the sensing behavior currently only involves the oxygen atoms, and it is unclear whether the hydroxyl functional group from water molecules will contribute to the Raman peaks observed experimentally and its role on the sensing performance.
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<th>Abbreviation</th>
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<tr>
<td>0D</td>
<td>zero-dimensional</td>
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<tr>
<td>1D</td>
<td>one-dimensional</td>
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<tr>
<td>2D</td>
<td>two-dimensional</td>
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<tr>
<td>3D</td>
<td>three-dimensional</td>
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<tr>
<td>AFM</td>
<td>antiferromagnetic</td>
</tr>
<tr>
<td>AGNR</td>
<td>armchair graphene nanoribbons</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin zone</td>
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<tr>
<td>CNTs</td>
<td>carbon nanotubes</td>
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<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
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<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DFPT</td>
<td>density functional perturbation theory</td>
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<tr>
<td>DGMO</td>
<td>direct-gap GMO</td>
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<tr>
<td>FLAPW</td>
<td>full-potential linearized augmented plane wave</td>
</tr>
<tr>
<td>FM</td>
<td>ferromagnetic</td>
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<tr>
<td>GGA</td>
<td>generalized gradient approximation</td>
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<td>GMO</td>
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<td>GNR</td>
<td>graphene nanoribbons</td>
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<td>GO</td>
<td>graphene oxide</td>
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<tr>
<td>IBZ</td>
<td>irreducible Brillouin zone</td>
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<tr>
<td>IGMO</td>
<td>indirect-gap GMO</td>
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<tr>
<td>IR</td>
<td>infrared</td>
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<td>Acronym</td>
<td>Description</td>
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<tr>
<td>LDA</td>
<td>local density approximation</td>
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<tr>
<td>LA</td>
<td>longitudinal acoustic</td>
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<tr>
<td>LO</td>
<td>longitudinal optical</td>
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<tr>
<td>MFP</td>
<td>mean free path</td>
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<tr>
<td>NEMS</td>
<td>nanoelectromechanical system</td>
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<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
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<tr>
<td>PZ</td>
<td>Perdew-Zunger</td>
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<tr>
<td>RGO</td>
<td>reduced graphene oxide</td>
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<td>STM</td>
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<td>in-plane transverse acoustic</td>
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