Physics and chemistry of oxidation of two-dimensional nanomaterials by molecular oxygen

Gaoxue Wang,† Ravindra Pandey†* and Shashi P. Karna‡

The discovery of graphene has inspired extensive interest in two-dimensional (2D) materials, and has led to synthesis/growth of additional 2D materials, generally referred to as ‘Beyond Graphene’. Notable among the recently discovered exotic 2D materials are group IV elemental monolayers silicene and germanene, group V elemental monolayer phosphorene, and binary monolayers, such as hexagonal boron nitride (h-BN), and molybdenum disulfide (MoS₂). Environmental effect on the physical and chemical properties of these 2D materials is a fundamental issue for their practical applications in devices operating under ambient conditions, especially, exposure to air often leads to oxidation of nanomaterials with significant impact on the functional properties and performances of devices built with them. In view of its importance, we present here a review of the recent experimental and theoretical studies on the oxidation of 2D materials focusing on the relationship between the oxidation process and the energy values which can be calculated by first principles methods. The complement of experiments and theory facilitates the understanding of the underlying oxidation process in terms of cohesive energy, energy barrier to oxidation and dissociation energy of oxygen molecule for 2D materials including graphene, silicene, germanene, phosphorene, h-BN, and MoS₂. © 2016 John Wiley & Sons, Ltd

INTRODUCTION

The discovery of graphene¹,² has inspired extensive interest in two-dimensional (2D) materials due to their unique properties and promising applications in electronics and optoelectronics, including transistors,³–⁸ sensors,⁹–¹³ energy storage and conversion devices,¹⁴–²⁰ and light-emitting devices.²¹–²⁷ Such wide range of applications has led to a fundamental question of the environmental effect on the physical and electronic properties of 2D nanomaterials. Of particular importance is the oxidation of materials in air, which can have significant impact on the functional properties and the performance of the devices built with them. Atomically thin 2D nanomaterials may exhibit high sensitivity to oxidation under ambient conditions.¹ However, silicene, the other group IV elemental monolayer, is found to quickly oxidize in air.³¹ Phosphorene, a recently isolated group V elemental monolayer, is found to be chemically unstable in air.³²–³⁴ Oxidation of 2D materials in ambient conditions can therefore present challenges in synthesis, characterization, and integration in active devices. Atomically thin 2D nanomaterials. Of particular importance is the oxidation of materials in air, which can have significant impact on the functional properties and the performance of the devices built with them. Atomically thin 2D nanomaterials may exhibit high sensitivity to oxidation under ambient conditions.¹ However, silicene, the other group IV elemental monolayer, is found to quickly oxidize in air.³¹ Phosphorene, a recently isolated group V elemental monolayer, is found to be chemically unstable in air.³²–³⁴ Oxidation of 2D materials in ambient conditions can therefore present Challenges in synthesis, characterization, and integration in active devices. Atomically thin 2D
nanomaterials exhibit high sensitivity to oxidation due to their large surface area, unsaturated valencies, and atomic-level defects among other factors. Thus, a detailed study of oxidation of 2D nanomaterials is of particular importance, both for gaining an enhanced understanding of their fundamental properties and for their potential applications in devices.

Since the field of 2D nanomaterials is growing rapidly, it is a daunting task to present a detailed review on all recently discovered materials. However, with a view to capture the underlying physics and chemistry, we present here a comprehensive review of the recent experimental and theoretical studies on oxidation of selected number of 2D materials that have attracted attention for their potential applications in nanotechnology. The considered 2D materials in this review include the group IV elemental monolayers, namely graphene, silicene, and germanene; the group V elemental monolayer, phosphorene; and binary monolayers, hexagonal boron nitride (h-BN), and molybdenum disulfide (MoS₂).

**THEORY**

Theoretical studies on oxidation of 2D nanomaterials have been mainly based on density functional theory (DFT) which has been a popular approach with remarkable success in addressing issues related to physics and chemistry of materials. DFT calculations can be successfully used to investigate atomic-level interaction of oxygen molecule with 2D materials, in addition to accurately establishing stable geometry and electronic structure, thus making it possible to relate the structure and chemistry of the materials to the oxidation process. In general, oxidation of 2D materials can be understood in terms of the energy barrier \( E_{\text{barrier}} \) to the transition state, and the dissociation energy \( E_{\text{diss}} \) of \( O_2 \) during the process. These energy values in turn depend on the strength of chemical bonds in the materials, which is related to the cohesive energy \( E_{\text{coh}} \). It is now possible to calculate the energy parameters \( E_{\text{barrier}}, E_{\text{diss}}, \) and \( E_{\text{coh}} \) with an accuracy of few meV with the use of the state-of-art DFT methods.

**Cohesive Energy of 2D Materials**

Cohesive energy, \( E_{\text{coh}} \), is defined as the energy released after the formation of a material from its constituting atoms and can be calculated as, \( E_{\text{coh}} = (N \times E_{\text{atom}} - E_{\text{total}})/N \), where \( E_{\text{total}} \) is the total energy of the 2D material, \( E_{\text{atom}} \) is the energy of a constituting atom, and \( N \) is the number of constituting atoms. \( E_{\text{coh}} \) is related to the strength of chemical bonds within the 2D lattice. The larger the value of \( E_{\text{coh}} \), the stronger the chemical bonds in the lattice. The values of \( E_{\text{coh}} \) of selected 2D materials obtained from DFT calculations are listed in Table 1. Note that the cohesive energy of some of the materials spans a wide range (around 1 eV) due to the use of different functional forms in DFT calculations.

Among the studied 2D materials, graphene and h-BN have the largest value of \( E_{\text{coh}} \) (greater than 7.0 eV/atom\(^{36–38,51,52} \)) originating from their planar structure with strong sp\(^2\) hybridized atoms forming \( \sigma \) bonds and the out-of-plane \( \pi \) bonds. Therefore, graphene and h-BN show good stability and resistance toward oxidation at ambient conditions. Silicene and germanene have relatively smaller value of \( E_{\text{coh}} \) in the range of 4.2–5.2 eV/atom\(^{38,42} \) and 3.4–4.2 eV/atom\(^{38,42} \), respectively, due to their buckled structure with slightly weaker sp\(^2\)–sp\(^3\) hybridized bonds. Therefore, both silicene and germanene are found to be sensitive to \( O_2 \).\(^{31} \) The cohesive energy of phosphorene is 3.3–3.8 eV/atom\(^{47,48} \), which is about half the value for graphene or h-BN. Enhanced sensitivity of phosphorene to oxygen is confirmed by experiments, which have demonstrated rapid degradation of this material.\(^{32,33,37,58} \) Overall, the cohesive energy is a general indicator of the strength of chemical bonds within the material.

**TABLE 1 | Calculated Lattice Constant, Cohesive Energy (\(E_{\text{coh}}\)), Energy Barrier (\(E_{\text{barrier}}\)), and the Dissociation Energy (\(E_{\text{diss}}\)) of O\(_2\) During Oxidation of 2D Materials**

<table>
<thead>
<tr>
<th>2D Monolayer</th>
<th>Lattice Constant (Å)</th>
<th>(E_{\text{coh}}) (eV/atom)</th>
<th>(E_{\text{barrier}}) (eV)</th>
<th>(E_{\text{diss}}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>2.46</td>
<td>7.7–7.9(^{36–38})</td>
<td>2.2–2.7(^{39–41})</td>
<td>0.7–2.2(^{39–41})</td>
</tr>
<tr>
<td>Silicene</td>
<td>3.87</td>
<td>4.2–5.2(^{38,42,43})</td>
<td>0.0(^{44})</td>
<td>–4.0 to –5.4(^{44})</td>
</tr>
<tr>
<td>Germanene</td>
<td>4.04</td>
<td>3.4–4.2(^{38,42})</td>
<td>0.6(^{45,46})</td>
<td>–2.3 to –2.5(^{45,46})</td>
</tr>
<tr>
<td>Phosphorene</td>
<td>4.62, 3.30</td>
<td>3.3–3.8(^{47,48})</td>
<td>0.1–0.5(^{49,50})</td>
<td>–4.0 to –4.5(^{49,50})</td>
</tr>
<tr>
<td>h-BN</td>
<td>2.51</td>
<td>7.1–7.9(^{51,52})</td>
<td>1.2–2.6(^{53})</td>
<td>1.1–2.2(^{53})</td>
</tr>
<tr>
<td>MoS(_2)</td>
<td>3.19</td>
<td>5.0–5.1(^{54,55})</td>
<td>1.6(^{56})</td>
<td>–</td>
</tr>
</tbody>
</table>

\(E_{\text{coh}}\) and \(E_{\text{barrier}}\) were calculated with either the Generalized Gradient Approximation with the Perdew–Burke–Ernzerhof functional (GGA-PBE) or the Local Density Approximation (LDA-DFT). The lattice constants were calculated at GGA-PBE level of theory.
bonds within the 2D material, thus its stability toward oxidation.

**Energy Barrier and Dissociation Energy During Oxidation**

In addition to the cohesive energy, the energy barrier ($E_{\text{barrier}}$) and the dissociation energy ($E_{\text{diss}}$) are quantities directly related to oxidation of the material which involves multiple reaction steps; the overall reaction rate is determined by the slowest step referred to as the rate-determining step for the process in air. Figure 1 depicts a simplistic schematics and not really suggestive of quantitative process associated with dissociation of an oxygen molecule on 2D materials. Here, $E_i$ is the energy of the reactants including the pristine 2D material and an O$_2$ molecule, $E_r$ is the energy of the transition state, and $E_f$ is the energy of the system after the dissociation of O$_2$ on the 2D lattice. The energy barrier (also known as the activation energy) during oxidation process is calculated as $E_{\text{barrier}} = E_r - E_i$, and the dissociation energy is $E_{\text{diss}} = E_f - E_i$. We note that $E_{\text{barrier}}$ and $E_{\text{diss}}$ are related to the fundamental interaction of O$_2$ with 2D materials, thus providing insightful information to their stability against oxidation.

The energy barrier, $E_{\text{barrier}}$ determines how fast oxidation of 2D materials could occur. According to the Arrhenius relationship, $K = Ae^{-E_{\text{barrier}}/k_BT}$, where $A$ is a preexponential term, $k_B$ is the Boltzmann constant, and $T$ is the temperature. A general rule of thumb is that reactions with energy barrier of 0.9 eV ($\approx 21$ kcal/mol) or less from DFT calculations will proceed readily at room temperature. The dissociation energy, $E_{\text{diss}}$ determines whether the oxidation process is exothermic or endothermic. A negative value of $E_{\text{diss}}$ implies the oxidation process to be exothermic, which is energetically favored. However, a positive value of $E_{\text{diss}}$ indicates the oxidation process to be endothermic for which external sources are necessary to provide the required energy during this process. Thus, a large energy barrier combined with a positive value of the dissociation energy provides resistance to a 2D material toward oxidation, thereby improving the conditions for their applications in devices operating in air. In contrast, a material with low $E_{\text{barrier}}$ (generally $< 0.9$ eV) and a negative value of $E_{\text{diss}}$ is expected to be oxidized readily. The energy barrier and the dissociation energy can be obtained using DFT calculations by considering a series of possible oxidation pathways. The calculated $E_{\text{barrier}}$ and $E_{\text{diss}}$ for the considered 2D materials are listed in Table 1. These values will be used to explain the experiments in the following sections.

**GROUP IV ELEMENTAL MONOLAYERS: GRAPHENE, SILICENE, AND GERMANENE**

**Graphene**

Graphene remains one of the most extensively investigated 2D materials and has offered a wealth of information on the exotic physics and potential technological applications. Graphene has a honeycomb structure with two carbon atoms in the unit cell. The carbon atoms are connected through $\sigma$ bonds with sp$^2$ hybridized character. The out-of-plane $p_z$ orbital forms the $\pi$ bands which endows the observed linear dispersion near Fermi level. Graphene can be synthesized by top–down strategy such as exfoliation from bulk graphite, or bottom–up strategy such as chemical vapor deposition (CVD). The readers can refer to a few comprehensive reviews on the fabrication, characterization, and application of graphene. Graphene shows extraordinary chemical stability in air at room temperature due to the robustness of the $\sigma$ bonds and the out-of-plane $\pi$ bonds. In fact, graphene has been used as a protection layer for metal substrates due to its excellent oxidation resistance. As shown in Figure 2, graphene acts as a molecular diffusion barrier thus preventing the reactive agent from reaching the metal underneath. Therefore, graphene coated Cu and Ni metals show very little visible change after annealing in air at...
200°C for 4 h, while the surface of uncoated metal changes dramatically (Figures 2(c)). Moreover, graphene can also provide short-term protection for metal exposed to an oxidizing aqueous solution of H$_2$O$_2$ (Figure 2(b)). While at temperature higher than 250°C, graphene starts to be reactive with O$_2$. Li et al. have shown oxidation induced strong hole doping in graphene at temperature from 200 to 300°C as revealed by Raman spectra, and the formation of etching pits at 500°C in O$_2$/Ar gas flow for 2 h as seen in Figure 3.

Recent theoretical studies have begun to provide an insight into the oxidation resistance of graphene. As seen in Table 1, the oxidation barrier of the defect-free graphene is approximately 2.7 eV. Moreover, the dissociation energy of O$_2$ molecule is 1.5 eV, which implies the oxidation process to be endothermic. A large energy barrier and a positive value of the dissociation energy of O$_2$ molecule imply that the defect-free graphene has excellent oxidation resistance at room temperature. Therefore, instead of forming a chemical bond, O$_2$ prefers to physically adsorb to graphene surface at room temperature, which results in the reversible doping of graphene after treatment in a different environment. However, at elevated temperatures, the thermal energy may overcome the energy barrier and trigger the irreversible oxidation of graphene. Both experiments and theory have shown that atomic O prefers to form epoxide group on graphene, i.e., an O atom covalently binds at the bridge site of two adjacent C atoms. The epoxide groups have the preference to align in a line resulting in the fragmentation of graphene layer into smaller pieces upon oxidation. It is interesting to note that the oxidized graphene fragments show rich spin structures, suggesting potential application in spintronic devices.

Defects also play an important role in oxidation of graphene. Defects are inevitable during the exfoliation or the growth process of 2D materials and have profound effects on their physical and chemical properties. Especially, the intrinsic defects, such as Stone–Wales (SW) defect, mono-vacancy, and divacancy with different configurations have been observed in graphene. The calculated energy profiles of O$_2$ dissociation of on the defect-free and
defective graphene is shown in Figure 4. It can be seen that O₂ dissociation on the defect-free graphene is endothermic (Route G) with the bridge site to be the preferred adsorption site for O atom. While O₂ dissociation on the defective graphene is highly exothermic with negligible barriers during the multistep process (Route I). Therefore, O₂ could chemically adsorb on the defective graphene. Based on the DFT calculation results, a two-step mechanism for oxidation of graphene has been proposed:

When exposed to O₂, (1) the bare vacancies in graphene are quickly saturated by ether and carbonyl groups and (2) the ether and carbonyl groups at the defect sites further activate the dissociation of O₂ leading to the formation of larger lactone groups, which could directly desorb CO or CO₂. This two-step oxidation process leads to the etching of graphene with the formation of pits, as observed in recent experiments.

Silicene
As the closest cousin of graphene belonging to the group IV elemental monolayers and being compatible with Si-based electronics, silicene has also attracted a great deal of attention from theorists and experimentalists. The stronger spin orbit coupling in silicene compared to graphene makes it a potential candidate for the study of quantum spin Hall effect (QSHE). The chemical bonds in silicene are different from those in the bulk; bulk Si is composed of sp³ hybridized Si atoms; whereas silicene has a low buckled structure with mixed sp²–sp³ hybridized Si atoms. Free-standing silicene is predicted to have linear dispersive band structure near Fermi level similar to that in graphene. The buckled structure and sp²–sp³ hybridized bonds impart novel physical and chemical properties to silicene differentiating it from graphene. Because of the nonexistence of a layered bulk counterpart, silicene cannot be isolated by exfoliation methods. Silicene has been grown by depositing Si atoms on Ag (111), ZrB₂ (0001), and MoS₂ substrates.

FIGURE 3 | Formation of pits in graphene. AFM images of oxidized single-layer (1L) and double-layer (2L) graphene: (a) oxidized at 500 °C for 2 h with P(O₂) = 350 torr, (b) oxidized at 600 °C for 40 min with P(O₂) = 260 torr. (Reprinted with permission from Ref 77. Copyright 2008 American Chemical Society)

FIGURE 4 | Oxidation of graphene with and without defects. Upper panel: The adsorption energy for dissociative O₂ adsorption on perfect basal plane of graphene (route G) and at a bare four-atom vacancy (route I); Lower panel: The corresponding geometries of the stable mediate adsorption structures along route I. (Reprinted with permission from Ref 40. Copyright 2009 Creative Commons Attribution 3.0 License)
Silicene is environmentally sensitive due to its mixed sp<sup>2</sup>–sp<sup>3</sup> hybridization.¹⁰⁸ As revealed by X-ray Photoelectron Spectroscopy (XPS) measurements (Figure 5), the epitaxial silicene on Ag (111) substrate suffers from serious oxidation only after 3-min exposure to air (Figure 5(d)). After one day exposure to air, silicene film completely transforms to silica (Figure 5(e)).³¹ The chemical instability of silicene in air limits its preparation to ultrahigh vacuum conditions and greatly hinders its applications in devices. Much efforts are needed on encapsulation at each step from material synthesis to fabrication of silicene-based devices. Recently, silicene-based field-effect transistor has been realized with in situ Al₂O₃ capping.⁷ Padova et al.¹⁰⁹ have recently shown 24 h stability of thick multilayer silicene in air without passivation, which is due to the formation of an ultra-thin oxide on the surface preventing the rest of silicene from oxidation.

The oxidation energy barrier is calculated to be zero on silicene surface,⁴⁴ and the oxidation process is exothermic with the dissociation energy of O₂ molecule to be −4.0 to −5.4 eV.⁴⁴ Therefore, silicene is expected to spontaneously oxidize in O₂. Atomic O prefers to bind to the bridge site of two neighboring Si atoms in the 2D lattice.⁴⁴,¹¹⁰,¹¹¹ The energy barrier for the O adatom moving on silicene is only 0.28 eV.¹¹⁰ Therefore, atomic O could easily penetrate the surface leading to significant oxidation of silicene.¹¹⁰ Interestingly, it is found that silicene shows low reactivity with pure O₂ when dosing up to 1000 L (Figure 5(c)).³¹,¹¹²,¹¹³ The discrepancy between theory and experiments implies that other ingredients, such as the defects in silicene or humidity in the air or both potentially play critical roles in oxidation of silicene. However, at present, oxidation of silicene remains poorly understood and needs further studies.

Germanene

Germanene is another analogue of graphene belonging to group IV elemental monolayers. The structure of germanene is similar to that of silicene with a buckled lattice.⁴² The Ge–Ge bonds in germanene show mixed sp<sup>3</sup>–sp<sup>3</sup> hybridized character.¹⁰⁰ The
The electronic properties of germanene have been extensively studied using DFT.\textsuperscript{42,114–117} Atomically thin germanene has been recently synthesized on Au (111), Al (111), or Pt (111) surface,\textsuperscript{118–120} while experimental reports on the interaction of germanene with O\textsubscript{2} are still lacking.

The oxidation energy barrier of germanene is calculated to be only 0.6 eV,\textsuperscript{45,46} and the oxidation process is predicted to be exothermic with the dissociation energy of \(-2.3\) to \(-2.5\) eV.\textsuperscript{45,46} The small cohesive energy of 3.4 to 4.2 eV\textsuperscript{38,42} indicates the Ge–Ge bonds in germanene are much easier to break than C–C bonds in graphene. Therefore, germanene is also expected to be sensitive to O\textsubscript{2} at room temperature.

GROUP V ELEMENTAL MONOLAYER: PHOSPHORENE

Phosphorene is one of the recently rediscovered group V elemental monolayers.\textsuperscript{6,121,122} A direct band gap, high carrier mobility, and anisotropic electronic and mechanical properties in phosphorene make it a promising candidate for applications in electronics and optoelectronics.\textsuperscript{123,124} Different allotropes of phosphorene have been predicted.\textsuperscript{125} The experimentally realized phosphorene, also sometimes referred to as black phosphorene, can be synthesized by mechanical\textsuperscript{121,126} or liquid exfoliation\textsuperscript{127,128} from its bulk counterpart, the black phosphorus, which is a layered material. In phosphorene, each P atom (with \(s^2p^3\) valence electron configuration) shares three of its valence electrons with the neighboring P atoms, while the remaining valence electrons form a lone pair at the surface. Electron lone pairs on P atoms in phosphorene enhance its sensitivity to adatoms and a few adsorbed molecules.\textsuperscript{129,130}

The exfoliated phosphorene samples quickly degrade in air.\textsuperscript{32–34,57} As shown in Figure 6(a), bump-like structures form on the surface of the sample shortly after exposure to air.\textsuperscript{57,130} These bumps grow in size and gradually deteriorate the sample after a few days.\textsuperscript{57,130} Finally, the sample transforms to phosphoric acid, forming large droplets (Figure (b)).\textsuperscript{57,130} Interestingly, the degradation of phosphorene is related to the presence of O\textsubscript{2}, H\textsubscript{2}O, and light. The degradation slows down when the sample is separately exposed to O\textsubscript{2}, H\textsubscript{2}O, and light (Figure 6(d) and (e)).\textsuperscript{57}

Recent DFT calculations have addressed the origin of the degradation of phosphorene in air. The calculations predict the energy barrier of O\textsubscript{2} dissociation on phosphorene to be less than 0.5 eV\textsuperscript{49} and the dissociation energy to be approximately \(-4.0\) eV.\textsuperscript{58} Therefore, phosphorene can easily oxidize with exposure to O\textsubscript{2}. The atomic O prefers to bind to the dangling site on the surface by forming P=O bonds.\textsuperscript{34,49,50,129} The oxidized species can further react with H\textsubscript{2}O forming phosphoric acid.\textsuperscript{58} The reaction of the oxidized species with H\textsubscript{2}O results in the formation of extra extrinsic defects in phosphorene,\textsuperscript{58} further promoting its photooxidation.\textsuperscript{131} This oxidation process leads to the fast degradation of phosphorene in air. Other phosphorene allotropes, such as

![Figure 6](https://example.com/figure6.png)
blue phosphorene are also expected to be unstable in air.58

HEXAGONAL BORON NITRIDE

Hexagonal boron nitride (h-BN) monolayer, also known as ‘white graphene,’ is iso-electronic to graphene.132,133 Both h-BN and graphene are comprised of sp² hybridized atoms with a planar honeycomb structure. The cohesive energy of h-BN is larger than 7.0 eV/atom,51,52 which reflects the presence of strong in-plane bonds. However, unlike graphene, the electronegativity difference between B and N leads to a partial electron transfer from B to N, thereby giving an ionic bonding character to h-BN.134 Moreover, unlike graphene, the h-BN sheets have a large band gap of approximately 6 eV, which allows them to be used as a dielectric in graphene-based electronics. Multilayered h-BN have also been widely used in optoelectronics.132 Large scale growth of h-BN has been achieved by CVD135–137 as well as mechanical exfoliation.138–140

Multilayer h-BN is quite stable in air at room temperature. Li et al.141 have recently demonstrated strong oxidation resistance of h-BN films. Although monolayer h-BN starts to oxidize at 700°C, it can sustain up to 850°C in air.141 Annealing in air for 2 h at temperatures below 840°C does not cause dramatic changes in the surface morphology of h-BN films.141

As seen in Figure 7(a), oxidative etching pits appear in h-BN monolayer after annealing in air at 850°C, and the monolayer burns out completely at 860°C.141 Bilayer and trilayer h-BN can sustain even higher temperature than the monolayer (Figure 7(b)–(e)).141 Thus, h-BN is suitable for high-temperature applications among the considered 2D materials. Strong oxidation resistance has also been reported for h-BN nanotubes, which are found to be stable in air up to 700°C.142 Because of the excellent oxidation resistance, BN sheets have been utilized as coating layers to protect polymers from oxidative corrosion.143

DFT calculations have predicted the O₂ dissociation energy barrier on h-BN to be greater than 1.5 eV.143 The O₂ dissociation process is endothermic with an energy increase of more than 1.2 eV.143 The high energy barrier and the endothermic process indicate a strong oxidation resistance of h-BN, which is consistent with experimental observation.141 The presence of point defects such as vacancies and SW defect are expected to reduce the oxidation resistance. Specifically, nitrogen vacancy has been predicted to reduce the oxidation energy barrier of h-BN nanotube to 0.8 eV,144,145 and metal adatoms or substrates are expected to catalyze the dissociation of O₂ on h-BN.146,147 Atomic O prefers to bind to the bridge site of B—N bond resulting in the elongation of the bond and a change in its nature from sp² to sp³ hybridization.53 The adsorbed O atoms tend to

---

**FIGURE 7** | AFM images of monolayer (1L), bilayer (2L), and trilayer (3L) h-BN after heating in air for 2 h. (Reprinted with permission from Ref 141. Copyright 2014 ACS AuthorChoice License)
form energy-favorable domains or chains leading to the formation of elongated etching pits and fracture on h-BN,\textsuperscript{53,148} which explains the experimental results.\textsuperscript{141}

**MOLYBDENUM DISULFIDE**

Transition metal dichalcogenides (TMDCs) are a large family of layered materials with unique electronic and optical properties.\textsuperscript{149} Bulk TMDCs are stacked together by a weak van der Waals (vdW) interaction which allows the exfoliation of the material down to monolayer.\textsuperscript{149–151} The properties of TMDCs depend on the structure and the stoichiometry leading to rich physics and chemistry in these materials.\textsuperscript{152,153} MoS\textsubscript{2} is a representative and most investigated member in the TMDCs family. Bulk MoS\textsubscript{2} is a semiconductor with an indirect band gap of 1.2 eV.\textsuperscript{154} The monolayer has a direct band gap of 1.8 eV, which makes it a promising candidate for next generation high-speed field-effect transistors (FETs) and optoelectronic devices.\textsuperscript{5,155–157} In monolayer MoS\textsubscript{2}, the Mo atoms are sandwiched between two layers of S atoms. Each Mo atom is surrounded by six neighboring S atoms. The p orbitals of S atoms hybridize with the d orbitals of Mo atoms, forming p–d hybridized ionic Mo–S bonds.\textsuperscript{158,159} Several experimental methods including mechanical exfoliation,\textsuperscript{5,8,152,160,161} CVD and metal–organic (MO) CVD\textsuperscript{66,162–165} have been used to fabricate MoS\textsubscript{2} monolayers.

MoS\textsubscript{2} shows good stability in air at room temperature. A few experiments and theoretical calculations have demonstrated that MoS\textsubscript{2} could be used as a passivation or protection layer to prevent oxidation of other materials.\textsuperscript{166,167} Oxidation of MoS\textsubscript{2} occurs at temperature higher than 300°C in air. Wu et al.\textsuperscript{168} have reported significant thinning and etching of MoS\textsubscript{2}, after 1 h annealing at temperature higher than 330°C in air (Figure 8(c), (d), (g), and (h)); At temperatures below 330°C, annealing in air does not cause significant change in its morphology (Figure 8(a), (b), (e), and (f)). The thinning and etching processes occur due to oxidation of MoS\textsubscript{2}, forming a transparent layer of MoO\textsubscript{3}.\textsuperscript{168,169} Long-time thermal annealing in Ar/O\textsubscript{2} mixture at temperatures higher than 320°C introduces oxidative etching pits in MoS\textsubscript{2}, which have been utilized to pattern MoS\textsubscript{2} sheets with well-oriented etching pits.\textsuperscript{168,170–172} Yamamoto et al.\textsuperscript{172} have shown that the edges of the triangular etching pits have the preference along zigzag direction as shown in Figure 9, and the etching is initiated at the native defect sites and grows laterally on the surface of MoS\textsubscript{2}.\textsuperscript{172}

The calculated oxidation energy barrier on MoS\textsubscript{2} is 1.6 eV.\textsuperscript{56} The large energy barrier explains the good stability of MoS\textsubscript{2} against oxidation at room temperature. Similar to graphene and h-BN, presence of atomic-level defects significantly alter the mechanism of O\textsubscript{2} adsorption in MoS\textsubscript{2}.\textsuperscript{56} Sulfur vacancies at the surface of MoS\textsubscript{2} is expected to reduce the oxidation energy barrier to 0.8 eV.\textsuperscript{56} Therefore, defect sites on MoS\textsubscript{2} surface exhibit high reactivity and are readily filled by oxygen atoms.\textsuperscript{56} These defective sites are also expected to act as the seeds that initiate the etching of MoS\textsubscript{2}. The theoretical calculation agrees very well with the experiment observation of the etching of MoS\textsubscript{2} starting at the native defect sites in the 2D lattice.\textsuperscript{172}

**CONCLUSION AND OUTLOOK**

In summary, we have presented a review of the recent experiments and theoretical studies addressing oxidation of selected 2D nanomaterials by molecular
O2. Depending on their structures and chemistries, oxidation of 2D nanomaterials has a wide variation. The combination of experiments and calculations reveals a significant role of the structure, chemical bonds and native defects in 2D materials for their practical applications in devices. With the advances in the exfoliation and synthesis techniques, several new atomically thin materials have emerged and the family of 2D materials continues to grow. Novel 2D materials hold great promise for future applications. But challenges remain in scaled up, high purity synthesis/growth, characterization, and integration of these materials into devices. Effective passivation or encapsulation methods need to be developed for 2D materials, such as silicene, germanene, and phosphorene, which are very promising for high-speed electronics, optoelectronics, and sensor applications, but found to be chemically unstable in the presence of oxygen. We hope this review encourages further investigations of the environmental effects on the structure and properties of 2D materials.

ACKNOWLEDGMENTS

This research was partially supported by a Cooperative Research Agreement (# W911NF-14-2-0088) with the Army Research Laboratory through Army Research Office. We thank Dr. J. Zabinski for his interest and helpful advice on this work.

REFERENCES


and electrical properties of chemical vapor deposition derived MoS2. ACS Nano 2014, 8:10551–10558.


