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Monolayer Alkali and Transition Metal Monoxides: MgO, CaO, MnO and NiO

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Two dimensional crystals with strong interactions between layers has attracted increasing attention in recent years in a variety of fields. In particular, the growth of single layer of oxide materials (e.g. MgO, CaO, NiO and MnO), over metallic substrates were found to display different physical properties than their bulk. In this study, we report on physical properties of single layer of metallic oxide materials and compare their properties with their bulk and other two dimensional (2D) crystals. We found that the planar structure of metallic monoxides are unstable instead the buckled structure are thermodynamically stable. Also, the 2D-MnO and NiO exhibit different magnetic (ferromagnetic) and optical properties than their bulk whereas band gap energy and linear stiffness found to be decreasing from NiO to MgO. Our findings provide novel insight into oxide thin-film technology applications.

1. INTRODUCTION

The successful isolation of graphene1 has motivated to exfoliate other layered materials such as e.g. MoS2, h-BN, and Phosphorene2,3 and to study the electronic, optical and mechanical properties of their mono and few layer 2D-crystals. However, preparing monolayer metal oxide materials is still a challenge, whilst they may have great potential applications in physics, chemistry and material science. In fact metal atoms prefer to form three-dimensional (3D) close-packed structures in contrast to graphite-like layered structures which have strong in-plane interaction and weak van der Waals interaction between layers.2 There are a few studies aimed to synthesis ultra thin metallic materials. For instance Duan et al.4 reported fabrication of poly-supported single-layered rhodium nanosheets using a facile solvothermal method, and Yin et al.5 studied the synthesis, formation mechanism, and mechanical property of multilayered ultrathin palladium nanosheets.

More recently, synthesis of various single layer to few layers of monoxide nano-crystals (MgO, CaO, CuO) were shown possible by trapping aqueous solution of corresponding salt in graphene nano-enclosures.6 Due to the light confinement and existence of large (1GPa) van der Waals pressure in these nano-enclosure trapped salt solutions were reached with water at room temperature, leading to 2D crystals of corresponding oxides. These findings lead us to propose the structure and electronic properties of monolayers of metal oxides.

Monolayer monoxides (MMO) with two different type of elements and cubic structure can form thin oxide films.7 These metal-oxide surfaces can exhibit catalytic properties useful for the fabrication of gas sensors, electronic and photonic devices.7−10 They also can be used in ceramics. Physical properties of metal oxide thin-films can be different from their bulk. Thin-films of MgO (1 to 5 layers) deposited over Ag can cause crumpling in the first layer due to the small lattice mismatch between substrate and the MgO cubic structure.8,11 Preparation of high quality crystalline calcium-oxide (CaO) films is more difficult as compared to that of MgO. The CaO thin-films have been grown on a Mo(001) support,12 and exhibited similar electronic and optical properties of bulk CaO.

On the other hand, antiferromagnetic (AFM) transition-metal monoxides, which can be grown as high-quality thin films on appropriate substrates, have relatively high AFM ordering temperature (Neel temperature).13,14 Their magnetic properties can be described by the Ising formalism and their insulating nature is due to the strong atomic electronic correlations. Anderson’s superexchange theory explains the interplay between charge and magnetic ordering.15 Thin films of metallic monoxide containing 3d transition metals like Mn, Fe, Co, or Ni have important applications in magnetic devices technology (see ref. 16 for a review on this topic). There is growing interest in the research on metal-oxides because of their fundamental electronic properties and their potential applications in different areas such as spintronics and spin valves based on the giant magnetoresistance.17−19

Manganese oxide (MnO) is an excellent and old model system used to investigate many kinds of magnetic effects at the surface of an AFM. Epitaxial growth of MnO films has been reported on Ag(001) substrate and Pd(100) single-crystal surface.20,21 Nickel oxide (NiO) thin-films (p-type oxide semiconductor) can also be deposited on a glass substrate using an inexpensive spray pyrolysis technique (SPT).16,22,23 Moreover, the NiO layer insertion between the active organic layer showed cell power conversion efficiencies as high as 5.2%.10 Recently, Ho et al.24 reported a main excitonic emission of 3.25 eV at 300 K and donor-acceptor-pair irradiations at lowered temperatures down to 10 K. NiO thin-film nanotower found to be an applicable material appropriate for UV luminescence and transparent-conducting-oxide applications.24

Despite a large number of studies on thin-films of MMOs, the electronic, structural and optical properties
of monolayer non-magnetic or ferromagnetic MMOs have not been explored. In this paper, we systematically study the electromechanical and optical properties of square lattice monolayer (which was experimentally observed by encapsulated bilayer graphene)\(^6\) of MgO and CaO as two nonmagnetic mono oxides and NiO and MnO as two AFM transition-metal monoxides. We found that a planar structure of MMO layer is unstable while the buckled structure is stable. Monolayer of MnO and NiO have a net magnetic moment with smaller electronic band gap as compared to monolayer MgO and CaO. The in-plane stiffness of NiO (MgO) is found to be largest (smallest) among the here investigated monolayers.

II. METHODS

Self-consistent density functional theory (DFT) calculations were used to study the electronic properties of MMOs employing the SIESTA software package.\(^25\) We used pseudopotentials that reproduce all-electron eigenvalues and excitation energies of multiple atomic configurations. The calculations were performed within the localized spin density approximation and LDA and PBE+D for Magnesium, Calcium, and the LDA(GGA)+U (Hubburd-corrected DFT energy functionals) for Nickel and Manganese, in conjunction with double-zeta polarized orbital for the basis sets and norm-conserving Troullier-Martins type pseudopotential for Magnesium, Calcium, Nickel, and Manganese atoms. In this work, we considered \(U_{ff} = U - J\) and therefore, the electronic properties of monolayers depend on the difference of both parameters. To calculate an accurate electronic bandstructure, the sampling of the Brillouin zone includes a fine \(18 \times 18 \times 1\) Monkhorst-Pack \(k\)-points grid for all structures studied. A similar fine grid was used to produce an accurate band structure. The geometry optimization was pursued until the convergence criterion was less than \(10^{-3}\) eV for total energy and less than 0.01 eV/Å for forces. The vibrational frequencies of MMOs are determined in the linear response framework. Dynamical matrices are computed at eight wave \(\bar{q}\) vectors in the irreducible wedge of BZ, i.e., on \(8 \times 8 \times 8\) grid.\(^26\)

Concerning the underestimation of the total energy and the energy gap by the LDA approach and the weakness of LDA in describing dispersion forces, we compare the total energy and other characteristics presented in Table I by considering PBE+Dispersion correction functional.

Optical properties of MMOs were computed using the BerkeleyGW (BGW) package based on first-principles many-body perturbation theory,\(^27\) see more details in refs.\(^28,29\). In summary quasiparticle excitation energies were computed as a first-order correction to DFT within the GG approximation of Perdew, Brueke, and Ernzerhof (PBE), with starting DFT-PBE eigenvectors and eigenvalues taken from the SIESTA and Quantum Espresso DFT package, which is compatible with the BerkeleyGW implementation. The frequency dependence of the dielectric function is obtained via the generalized Plasmon-pole (GPP) model and Optical excitations energies by inclusion of electron-hole interaction from the solution of the Bethe-Salpeter equation (BSE).\(^27,30\)

The supercell with lattice vector (z direction) set to 40\(a\) to avoid interactions with periodic images and contains a 99\% of the charge density and the Coulomb interaction cut off radius was adjusted at distances larger than half of the unit cell size. The supercell dimensions are \(12 \times 12 \times 40\) \(\AA\). The BSE sum was computed using \(8 (16)\) valence\(\times (8 (16))\) conduction states for MMOs. To build the dielectric function and self-energy, the total number of states are 2394 for monolayers, spanning an energy range greater than 35 eV above the highest occupied state. The dielectric function plane wave’s cutoff is 160 eV.

Subsequent to our GW calculations, the BSE is solved within the Tamm-Dancoff and static approximations to compute the complex transverse dielectric function, \(\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)\). The absorption coefficient, \(\alpha(\omega)\) is given by:\(^31\)

\[
\alpha(\omega) = 2\omega \sqrt{1/2 - \epsilon_1(\omega) + \sqrt{\epsilon_1(\omega)^2 + \epsilon_2(\omega)^2}}
\]

where \(\omega\) has units of energy (in atomic units).

III. BUCKLED STRUCTURE

In this section we perform DFT calculations for determining the lattice structure of MMOs. Each studied monolayer (2D-XO) consists of a \(\{100\}\) plane of MMOs crystals where \(X=Mg, Ca, Mn\) and \(Ni\). We used a unit cell with 16 atoms and applied periodic boundary conditions. We found that the optimized buckled structure has lower energy than a planar 2D-XO(100). The buckled structure refers to the non-planar lattices where e.g. a Mg (Ca, Ni, and Mn) atom in the MgO lattice is in a different plane than nearest Mg atoms \(z_{Mg} = +0.3\) and even different plane than nearest Mg atoms \(z_{Mg} = -0.3\).

The variation of the total energy with lattice constant for planar and buckled MgO(100) are shown in Fig. 1(a). For 2D-MgO(100) (buckled structure) the lattice constant found to be 3.9\(\AA\) which is close to the lattice constant of bulk MgO\(^32\) (4.191\(\AA\)) and is 1.3\% larger than the lattice constant of MgO Nanosheets\(^33\) (3.85\(\AA\)). The out of plane height in the buckled structure is \(\pm 0.3\)\(\AA\) for Mg atoms and 0\(\AA\) for O atoms which are in agreement with results reported for MgO nanosheets.\(^34\) For other MMOs the buckling heights and lattice constants are listed in Table I. The exceptional case is MnO, where we found that O atoms also moves down and up, which is similar to armchair configuration of fluorinated or hydrogenated graphene.\(^34\) The structural deformation in the e.g. Mg-O bonds (the buckling effect) is due to minimizing the repulsion between \(2p\) orbital of O atom and \(3p, 3d\) orbitals
of Mg atom. This improves the overlap between these orbitals.

In order to show that the buckled 2D-XO(100) is a stable 2D material, we performed phonon band structure calculations. A typical phonon band structure at high symmetry points for both planar and buckled structures of 2D-MgO(100) are shown in Figs. 1(b,c). There are twelve phonon branches including three acoustic branches with zero frequency at the zone center, and nine optical branches. It is seen that for the planar 2D-MgO(100) one acoustic and two optical phonon bands have imaginary frequencies. However, in the buckled structure (Fig. 1(c)) all the phonon modes have positive frequencies, which confirms the buckled structure is stable. It is interesting to note that the phonon dispersion frequency for the buckled structure is similar to that of bulk MgO.\(^{35-37}\)

We also performed finite temperature \textit{ab initio} molecular dynamics simulations (MD) for buckled structures with the same unitcell (36 atoms) and found that this structure is thermodynamically stable at room temperature during a long time MD simulations (1 ns). Therefore hereafter our results are presented for the buckled 2D-XOs.

Notice the (optical and acoustic) phonon bands here are different than those for other 2D materials, e.g. graphene. The phonon frequencies (900cm\(^{-1}\)) of MgO is lower than the optical frequency in graphene (1600 cm\(^{-1}\))\(^26\) as a result of ionic bound between Mg and O atoms. However, the results are similar to the phonon spectrum of chlorographene, where the phonon spectrum is softened (1061 cm\(^{-1}\)) due to the saturation of C atoms with heavy Cl atoms. This is unlike that of for the C-H bond in graphene and C-F in fluorinated graphene.\(^{38-40}\)

\section{IV. ELECTRONIC STRUCTURE}

\subsection{A. MgO}

In Figs. 2(a-d) we compare the electronic band structure and corresponding density of states (DOS) and projected density of states (PDOS) of the buckled 2D-MgO(100) and bulk MgO acquired by DFT-PBE results. As a first remark, both have direct band gaps and the Fermi energy of the bulk is lower than that of the buckled 2D-structure. The valence bands (VB) for both structures have less variation in the \(k\)-space demonstrating the localized electronic states.\(^41\) The lowest conduction band (CB) exhibits significant curvature in the \(k\)-space. The upper conduction bands are flat for the buckled 2D-MgO(100) as compared to the bulk MgO. The band gap energy estimated to be 3.82 eV (6.1 eV) for the 2D-MgO(100) (bulk MgO). The band gap for the buckled structure is comparable with that of reported by Zhang \textit{et al.}, i.e. 4.23 eV\(^23\) for MgO nanosheets. The two-fold degeneracy at top of the CB in the bulk MgO is removed in the 2D-MgO(100) as compared to bulk MgO which is due to the broken symmetry in the low dimensional system.

\subsection{B. CaO}

The electronic band structure of CaO and the corresponding DOS and PDOS are shown in Fig. 3(a-c) acquired by DFT-PBE results. In Fig. 3(d) we depict the side and top views of the buckled 2D-CaO(100). We found that the 2D-CaO(100) have a direct band gap of 2.03 eV while bulk CaO, with cubic rocksalt structure, exhibits insulator behavior with a wide band gap of 7.7 eV.\(^42,43\) This is consistent with experimentally observed decrease in the band gap of CaO thin-film\(^44,45\), i.e. Cui \textit{et al.} have found the band gap of CaO thin-film grown on Mo(100) to be 7.1 eV using a low-temperature scanning tunneling microscopy technique.\(^44\) Notice here our finding (2.03 eV) is for a monolayer of CaO which is very thinner than those thin-film studied in refs.\(^44,45\). Therefore, because of small indirect band gap one can conclude that monolayer of CaO(100) can show semiconducting properties.

Figs. 2(b),(d) and Fig. 3(c) show that the CB is significantly a combination of cationic Mg (Ca) 3s, 3p, and 3d states, while VB is drastically dominated by anionic O 2p states, as expected for an ionic oxide.

\section{V. MNO AND NIO}

The buckled 2D-MnO(100) and 2D-NiO(100) found to have indirect band gap which are about 0.88 eV and 1.21 eV, respectively. The latter is in contrast to the well known direct band gap of bulk MnO and NiO.\(^46-48\)

In Fig. 4 and Fig. 5 the electronic band structure of the buckled 2D-MnO(100) and 2D-NiO(100) (for spin-up electrons), projected density of states (PDOS) and corresponding DOS diagrams for both spin-up and spin-down electrons are shown, acquired by DFT-PBE results. Figures 4(c), 5(c), PDOS reveal that VB is dominated by 3d states of cationic Mn and Ni. The electronic states for the spin-up and spin-down are different resulting in magnetic moments of 5\(\mu_B\) and 2\(\mu_B\) for 2D-MnO(100) and 2D-NiO(100), respectively. The top and side views of the buckled structure of the 2D-MnO(100) and 2D-NiO(100) are depicted in Fig. 4(d) and Fig. 5(d), respectively. As already mentioned the out of plane of atoms in the buckled structure of 2D-MnO(100) is different than the others, i.e. some Mn atoms are in the same plane of O atoms.

In fact antiferromagnetic properties occur among 3D-bulk of transition metal compounds, especially oxides such as NiO and MnO, i.e. the Mn\(^{2+}\) and Ni\(^{2+}\) ions are in one (111) plane have a parallel spin alignment with each other and the ions in an adjacent (111) plane have antiparallel spin alignment. For bulk MnO and NiO, we found zero magnetic moment (AFM) while for 2D-MnO(100) and 2D-NiO(100) the magnetic moment...
found to be $\sim 5\mu_B$ and $\sim 2\mu_B$ per unit cell (indicating FM state), respectively.

The comparison of the total density of states of 2D-MnO(100) and 2D-NiO(100) for different values of U with the LDA+U approach plotted in Figs. 6(a-h). These figures manifest that the LDA+U band gaps in MnO and NiO increase nonlinearly with increasing U, as changes in the p-d hybridization. Our results are in line with reported U dependence of monoxides band gaps reported in the previous works$^{19,50}$

Yamijula, et. al,$^{51}$ reported that graphene quantum dots with edges doped with boron nitride show spin-dependency of HOMO-LUMO gap, because of the intrinsic electric-field (charge-transfer between B, N) present in the system.$^{51}$ They proposed, if the spin-degeneracy at the zigzag-edge can be broken by using methods like doping,$^{62}$ external electric field,$^{53}$ strain,$^{54}$ and substitution,$^{51,55}$ the system will create magnetic moments. To discover the origin of the magnetic moment of 2D-MnO(100) and 2D-NiO(100), a simulated scanning tunneling microscopy (STM) image was obtained for 2D-MnO(100) and 2D-NiO(100) using a numerical STM tool for probing the electronic states and states mixing. Figure 7 gives two perspectives of the topographic simulated STM images calculated above the structures. Computing a STM image of MnO and NiO reveal subtle information on the variation of their electronic properties and the extra electronic states, with green protrusions related to negative charge accumulation on MnO and NiO in consistency with broken local symmetry (local spin rotation) due to the computed DFT electrical dipole moment (intrinsic electric field) of 0.13 Debye for 2D-MnO(100) and 0.076 Debye for 2D-NiO(100). The magnetic superexchange interaction in manganites depends on the MnOMn bond angle.$^{56,57}$ Orbitally degenerate structures will undergo a geometry and electronic states distortion that lift the degeneracy. The main physical reason for the appearance of the FM state in monolayer MnO and NiO is as follows. For bulk MnO (and NiO), because Mn$^{2+}$ (Ni$^{2+}$) is connected at 180 to the bridging non-magnetic O$^{2-}$, there is a coupling between two next-nearest neighbor Mn$^{2+}$ (Ni$^{2+}$) through O$^{2-}$ resulting in an antiferromagnetic coupling. However, when the cation-aniom-cation bond angle deviates from 180 the interaction can be ferromagnetic where the direct and indirect exchange mechanisms compete with each other. The 2D-MnO and NiO are found to be non-planar in our calculations corresponding to the latter situation and therefore we expect no antiferromagnetic state. Our results show a larger magnetic moment for MnO as compared to NiO which can be attributed to the larger deviation from 180 in MnO. This symmetry breaking at the plane of (100) of monolayer monoxides induces a surface ferromagnetic layer, in consistence with previous reports.$^{58}$ Moreover, we computed Mulliken charge distribution to figure out the ferromagnetic origin of 2D-MnO and NiO monolayers. Figures 8 (a,b) show the corresponding Mulliken charge distribution obtained by using the spin polarized calculations. The black and gray bars show the charge of spin-up and spin-down, respectively (for the Mn and Ni atoms). The empty and the filled blue bars indicate the charge of spin-up and the spin-down, respectively, (for the O atoms) which are almost equal. It can be seen that the charge difference between the spin-up and spin-down of Mn and Ni atoms are $5\mu_B$ and $2\mu_B$, respectively. However, the charge difference between the spin-up and spin-down state of O atoms in MnO are zero, hence O atoms do not contribute to the magnetic moments of 2D-MnO(100), while for NiO they are not zero.

The splitting of projected density of states (PDOS) of the Mn and Ni atoms are shown in Fig. 8 (c,d). The solid and dashed lines refer to the PDOS of the spin-up and the spin-down which have different energy and PDOS. The different magnetic moments of 2D-MnO(100) and 2D-NiO(100) are simply related to the number of unpaired electrons in their d-orbitals.

### A. Optical Properties

Single photon quantum emission from two dimensional materials at room temperature has been studied by Tran and his collaborators which reveal unprecedented potential for nanophotonics and quantum information processing.$^{62}$ They simulated the optical response of defects in two dimensional sheets by using density functional theory and by calculating the imaginary dielectric tensor.$^{62}$ Meanwhile, for the solar cell applications, a photocatalytic material should have wide absorption range of the solar and visible energy in the range e.g. 1.5-3.5 eV and band gap between in the range 2-3 eV.$^{63}$ The electronic band structure of 2D-MgO(100) and bulk MgO are shown in Figs. 2(a,c). It was found that the monolayer MgO has smaller direct band gap than bulk MgO.

The optical absorption spectrum obtained by calculating the real and imaginary part of the complex dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) using Eq. (1). In Figs. 9 (a-d) we compare the optical absorption spectrum of 2D-MgO(100) and bulk MgO. The solid lines (dashed lines) refer to the excitation; interacting electron-hole (non-interacting electron-hole). For the buckled 2D-MgO(100) we obtain the first peak at 1.58 eV and the second peak at 3.87 eV which are very close to the visible light range (i.e. 1.64-3.2 eV), see Fig. 9(a).$^{64}$ The optical absorption spectrum indicates a blue-shift light absorption range for MgO bulk due to its larger electronic band gap.

We estimate the GW gap using GW calculations (see Figs. 9(b,d)). The GW gap for the 2D-MgO(100) (bulk) found to be $\sim 3.3eV \sim 9 eV$.

The absorption spectrum of the 2D-CaO(100), 2D-MnO(100) and 2D-NiO(100) are shown in Figs. 9(e-p). Despite small direct band gap of 2D-CaO(100) it has no any absorption peak in visible light range. An absorption occurs at 2.5 eV for 2D-MnO(100) which is
relevant to the results reported by Pandey et al. 59, where they have reported optical properties of synthesized MnO nanoparticles (colloidal solution) using UV-visible absorption spectroscopy. The absorption spectrum of 2D-NiO(100) contains several peaks in the range [1.5-3] eV, which are perfectly in the visible light range. This is in agreement with the absorption spectrum of NiO nanoparticles found by Hosny et al. 60,61, where several peaks in the visible light range have been reported. The GW gap for the 2D-MnO(100) and 2D-NiO found to be 1.7 eV and 1.9 eV, respectively, which are promising for photovoltaic applications. Jiang et al. studied optical properties of crystalline NiO films, prepared by electron beam deposition on quartz substrate 61 and found a strong ultraviolet emission at 377 nm for cubic structure along the (111) plane. As seen in Fig. 9o, the absorption spectrum for bulk NiO has peaks in infrared and ultraviolet range.

VI. ELASTIC PROPERTIES

Here we investigate the mechanical properties of 2D-XO(100). The elastic properties of these structures can be conveniently characterized by their linear response to an external in-plane stress, i.e. estimating the in-plane stiffness ‘C’ which is equivalent to 2D-Young’s modulus. Using S as the equilibrium area of the unit cell of a typical 2D-XO(100) structure, the in-plane stiffness is obtained as $C = \frac{\delta^2 E}{\delta \epsilon^2}$, where $E_s$ is the total energy and $\epsilon$ is the uniaxial strain. Calculating the variation of the total energy with respect to the applied in-plane strain gives the in-plane stiffness, see Fig. 10(a). The in-plane stiffness for four 2D-XO(100) are listed in Table I. We also found a linear decrease in the electronic band gap with respect to the applied strain (Fig. 10(b)). The largest (smallest) the in-plane stiffness found for 2D-NiO(100) (2D-MgO(100)). The energy gap variation with strain is also maximum for NiO(100).

VII. DISCUSSION AND CONCLUSIONS

Reducing size can change the magnetic and optoelectronic properties of the thin-films of MMOs which are considerably different from those of bulk. The so called Mermin-Wagner theorem states that the systems with short-range interactions in one or two dimensions, because of intrinsic thermal fluctuations, cannot develop long-range magnetic order at finite temperature. 64 The Mermin-Wagner theorem is invoked to explain the absence of long-range order at finite temperatures. Strictly speaking, this would mean, however, that the Neel temperature is zero. There has been a long discussion about the importance of the Mermin-Wagner theorem for long-range order in 2d materials (rippling of graphene), and it has been concluded that the Mermin-Wagner theorem is not important at relevant length scales. 65

Consequently for instance a significant reduction in the magnetic transition temperature is expectable in AFM oxides in low-dimensional geometries 66,67. Here we propose the thinnest MMOs (the one atom layer) is stable and found a long range magnetic order for 2d allotrope of transition metals. We showed that the (100) lattice structure of MgO, CaO, MnO and NiO are stable that are not flat. We found the stable structure of the metallic monoxides are buckled structure with buckling height less than 1Å and with different electronic and optical properties than those of their bulk.

In the bulk of transition metal oxides (MnO and NiO) as already mentioned cations are located in the (111) planes. The latter creates two opposing magnetic moment sublattices and consequently zero total magnetic moment. The cations in different sublattices are connected by 90° oxygen bonds resulting in the AFM order. The 2D allotrope of MnO and NiO in the (100) found to have magnetic moments of $5\mu_B$ and $2\mu_B$, respectively, as a consequence of broken symmetry of local electrical density of states. On the other hand, since bulk NiO and bulk MgO have the same lattice structure with infinitesimal lattice mismatch (0.2%), the high-quality NiO thin-films (25ML) can be grown on MgO(100) crystal 68. MnO and NiO can also be deposited on Ag(100) single crystal and exhibits the thickness-dependent AFM anisotropy. 69,70 By using ab-initio calculations, we found the lattice mismatch between 2D-NiO(100) and 2D-MgO(100) is even smaller (0.15%) which is promising for synthesis NiO-MgO bilayer and multilayer.

Furthermore, it is well known that a semiconductor with band gap between 1.0 eV and 1.5 eV, or near-infrared light, have the highest efficiency for potential applications in solar cell. The solar cells made of thin-film technologies has not yet been commercially developed and they are still in the research phase. Here we found that the GW gap (GW/BSE) is about 2.65 eV and 2.57 eV for the 2D-MnO(100) and 2D-NiO(100), respectively. There are several peaks in the absorption spectrum of the 2D-NiO(100) which are located at the visible light region. The latter is promising for fabricating new thin-film based photovoltaics solar cells. In summary, these findings of monolayer of metallic monoxides have important applications in thin-film technologies, nano-electronic, spintronics and solar cells using 2D materials with tunable opto-electro-thermo-mechanical properties using different number of layers.

Finally, we discuss whether or not these monolayer crystals can be stable in nature. Indeed the synthesis of isolated MMOs is difficult, however MMOs deposition over inert substrates or encapsulating them by graphene or other 2D materials membrane can be realized. Recently, we proposed that by using graphene bilayer as a scaffold synthesize of silicene with electronic properties decoupled from the substrate would be possible. 71 The recent observation of conversion of graphene encap-
sulated aqueous salt solution to 2D crystals\(^6\) of corre-
sponding metal oxide is an encouraging route to follow.

TABLE I: Comparison of the physical properties of the buckled monolayer-XO(100) (X = Mg, Ca, Mn, Ni) with those for graphene, h-BN and MoS$_2$, i.e. lattice constant (a), bond distance X-O (d), the buckling height ($\delta$), electronic band gap energy ($\Delta$), magnetic moment ($\mu_B$), the in-plane stiffness (Y). The numbers inside brackets are the experimental results for bulk MMOs. In the LDA+U and GGA+U, results for U=1 are presented.

<table>
<thead>
<tr>
<th>2D-crystal</th>
<th>a (Å)</th>
<th>d (Å)</th>
<th>$\delta$(Å)</th>
<th>$E_T$ (eV)</th>
<th>$\Delta$ (eV)</th>
<th>M ($\mu_B$)</th>
<th>Y (J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene (LDA)</td>
<td>2.46</td>
<td>1.42</td>
<td>0</td>
<td>-81.13</td>
<td>0</td>
<td>0</td>
<td>335</td>
</tr>
<tr>
<td>h-BN (LDA)</td>
<td>2.49</td>
<td>1.45</td>
<td>0</td>
<td>-96.65</td>
<td>5.5 [5-7$^{22}$]</td>
<td>0</td>
<td>300</td>
</tr>
<tr>
<td>MoS$_2$ (LDA)</td>
<td>3.18</td>
<td>2.34</td>
<td>$\pm$1.6</td>
<td>-140.4</td>
<td>1.76 [1.23$^{23}$]</td>
<td>0</td>
<td>378[343$^{24}$]</td>
</tr>
<tr>
<td>MgO (LDA) (PBE+D)</td>
<td>3.9</td>
<td>1.95</td>
<td>$\pm$0.3</td>
<td>-268.69</td>
<td>3.82[6.1]</td>
<td>0</td>
<td>118 [248$^{75}$]</td>
</tr>
<tr>
<td>CaO (LDA) (PBE+D)</td>
<td>4.6</td>
<td>2.3</td>
<td>$\pm$0.4</td>
<td>-285.1</td>
<td>2.03 [4.66]</td>
<td>0</td>
<td>346 [224$^{13}$]</td>
</tr>
<tr>
<td>MnO (LDA+U) (PBE+D)</td>
<td>4</td>
<td>2</td>
<td>$\pm$0.5</td>
<td>-429.67</td>
<td>0.88 [3.6]</td>
<td>5[0]</td>
<td>470[245$^{13}$]</td>
</tr>
<tr>
<td>NiO (LDA+U) (GGA+U)</td>
<td>3.84</td>
<td>1.92</td>
<td>$\pm$0.25</td>
<td>-712.77</td>
<td>1.21 [3.8]</td>
<td>2[0]</td>
<td>687 [388$^{13}$]</td>
</tr>
<tr>
<td>NiO (LDA+U) (GGA+U)</td>
<td>3.95</td>
<td>1.97</td>
<td>$\pm$0.25</td>
<td>-728.69</td>
<td>1.45</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE II: Comparison of the energy gap of monolayer MnO(100) and monolayer NiO(100) with GW gap for different values of U with the LDA+U and GGA+U approaches.

<table>
<thead>
<tr>
<th>Energy gap (eV)</th>
<th>MnO (LDA+U)</th>
<th>GGA+U</th>
<th>NiO (LDA+U)</th>
<th>GGA+U</th>
</tr>
</thead>
<tbody>
<tr>
<td>U = 1</td>
<td>0.88</td>
<td>1.18</td>
<td>1.21</td>
<td>1.45</td>
</tr>
<tr>
<td>U = 2</td>
<td>1.33</td>
<td>1.56</td>
<td>2.04</td>
<td>2.31</td>
</tr>
<tr>
<td>U = 3</td>
<td>1.95</td>
<td>2.18</td>
<td>2.67</td>
<td>2.83</td>
</tr>
<tr>
<td>U = 4</td>
<td>2.37</td>
<td>2.65</td>
<td>2.96</td>
<td>3.34</td>
</tr>
<tr>
<td>GW gap</td>
<td>2.03</td>
<td>2.57</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIG. 1: (Color online) The variation of energy with lattice constant of monolayer MgO(100) calculated by using LDA, for (a) the planar and the buckled structures. Phonon dispersion spectra of the planar (b) and the buckled (c) structures. The red-dashed lines indicate imaginary frequency region for planar MgO(100).

FIG. 2: (Color online) The electronic band structure of spin-up, total density of states (DOS) and projected density of states (PDOS) of (a,b) the buckled monolayer MgO(100) and (c,d) bulk MgO, as obtained from DFT-PBE.
FIG. 3: (Color online) (a) The electronic band structure of spin-up, (b) total density of states (DOS) and (c) projected density of states (PDOS) of the buckled monolayer CaO(100). (d) The side and top views of the buckled structure of monolayer CaO(100), from DFT-PBE.

FIG. 4: (Color online) (a) The electronic band structure of spin-up, (b) total density of states (DOS) and (c) projected density of states (PDOS) of the buckled monolayer MnO(100). (d) The side and top views of the buckled structure of monolayer MnO(100), from DFT-PBE.
FIG. 5: (Color online) (a) The electronic band structure of spin-up, (b) total density of states (DOS) and (c) projected density of states (PDOS) of the buckled monolayer NiO(100). (d) The side and top views of the buckled structure of monolayer NiO(100), from DFT-PBE.

FIG. 6: (Color online) Comparison of the total density of states of monolayer MnO(100) (a,c,e,g) and monolayer NiO(100) (b,d,f,h) for different values of $U_{eff}$ obtained with the LDA+U approach.
FIG. 7: (Color online) Simulated STM images from top, for MnO(100) (a) and for NiO(100) (b). STM images were calculated with $I = 0.1$ nA and $V_b = -0.5$ V.

FIG. 8: (Color online) Mulliken charge distribution for (a) Mn, O and (b) Ni, O atoms. Black and gray bars indicate the charge of spin-up and spin-down of Mn and Ni atoms, and the empty and filled blue bars indicate charge of spin-up and spin-down of the O atoms. The spatial spin density distribution for Mn and Ni ($\rho \uparrow - \rho \downarrow$) is also plotted (Mn: spin-up, blue; spin-down, green; Ni: spin-up, violet, spin-down, pink).

. (c), (d) Splitting of PDOS of 3d-orbital for spin-up and spin-down of MnO(100) and NiO(100).
FIG. 9: (Color online) (a) Comparison of the optical absorption spectrum computed for the XO(100) mono layers (X = Mg, Ca, Mn, Ni) and their bulk in two different phases; for interacting (solid line) and for non-interacting electron-hole case (dashed line), i.e. (a-b) is the results for monolayer MgO(100) and (b,c) is for bulk MgO and etc.

FIG. 10: (Color online) The variation of the total energy (a) and electronic band gap with applied strain (b).