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Electro- and Opto-Mutable Properties of MgO Nanoclusters Adsorbed on Mono- and Double-Layer Graphene

Farzaneh Shayeganfar^{1,2}, Javad Beheshtiyan^{2,3}, Mehdi Neek-Amal^{2,3}, and Rouzbeh Shahsavari^{1,4,5*}

¹Department of Civil and Environmental Engineering, Rice University, Houston, TX 77005

²Institute for Advanced Technologies, Shahid Rajaei Teacher Training University, 16875-163, Lavizan, Tehran, Iran.

³Department of Physics, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium

⁴Department of Material Science and NanoEngineering, Rice University, Houston, TX 77005

⁵Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, TX 77005

*Corresponding author email: rouzbeh@rice.edu

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Abstract. Inspired by recent experiments, trapping molecules in 2D materials are gaining increasing attention - due to their unique features modulating electronic and optical properties of 2D materials – which call for fundamental understanding and predictive design strategies. Herein, we focus on mono- and double-layer graphene encapsulating various MgO clusters and explore their diverse electronic and optical properties using a number of high-level first-principles calculations. By correlating the stability of adsorption, geometry, charge transfer, band structures, optical absorption spectrum, and the van der Waals pressure, our results decode various synergies in electro-and opto-mutable properties of MgO/graphene systems. We found that 2D-MgO flakes on graphene layers exhibit surface polarization effects - in contrast to their isolated neutral flakes – and show a significant charge transfer from graphene to n-doped flakes,

breaking the symmetry of graphene layers. We obtained van der Waals pressure of ~ 0.7 (0.9) GPa on bilayer graphene encapsulating MgO nanoclusters, which match extremely well with experiment. While there is one quantum emission in the visible light region for the single MgO flake, a wide range of visible light is accessible for MgO on mono- and double-layer graphene. Overall, these findings provide new physical insights and design strategies to modulate 2D materials with several applications in optoelectronics while significantly broadening the spectrum of strategies for fabricating new hybrid 2D heterostructures by encapsulating external molecules.

1- Introduction

Layered crystals and van der Waals (vdW) assembly of two-dimensional (2D) quantum confinement are an emerging area of materials research for energy conversion and information Technologies.^{1,2} Trapping molecules between 2D materials (heterostructures) have gained intense attentions for their unique features.³ Heterostructures of graphene and hexagonal boron-nitride (h-BN) have attracted much attention because 2D h-BN acts as a tunnel barrier for spin injection into graphene while graphene has spin diffusion at room temperature and ideal medium for long distance spin transport.^{4,5,6,7,8,9} Furthermore, stacked heterostructures via graphene could generate new spintronic devices through long spin-diffusion lengths in graphene and spin-orbit and exchange interactions.¹⁰

From a nanocluster and thin film perspectives, metal-oxide thin films such as MgO display wide range of technological applications such as gas sensors or catalysis,^{11,12} and layer-by-layer

growth to design oxide heterostructures.^{13,14} Volmer *et al.* reported the influence of MgO barriers on spin and charge transport properties by fabricating both single and bilayer graphene spin-valve devices with variable contact resistance of MgO/Co electrodes.⁵ Dalai *et al.* fabricated MgO-based double barrier magnetic tunnel junctions for synthesizing CoFeB/Ru/CoFeB free layer as antiferromagnetism.¹⁵ The rich behavior of MgO heterostructures arises from a series of interactions at the interfaces between spin, charge, orbital and lattice degrees of freedom. These complex interactions can be modified at interfaces through the charge transfer, strain, electrostatic coupling and local symmetry breaking.¹³

Heterostructures composed of 2D materials such as graphene, boron-nitride (BN) and MoS₂ are fabricated via layer by layer assembly where the layer interactions are dominated by the van der Waals (vdW) interactions. In this regard, Al Balushi *et al.*, synthesized 2D gallium nitride by a migration enhanced encapsulated growth technique to discover a new phase of 2D materials.¹⁶ They demonstrated experimentally and theoretically that buckled 2D gallium nitride encapsulated between graphene layers and silicon carbide is energetically more favorable than the planar and shows direct band gap suitable for optoelectronic devices. More precisely, the stability of cleaved wurtzite surfaces is affected by surface passivation. Two types of freestanding monolayer hexagonal group-III nitride structures, planar and buckled are predicted to be stable. Based on density functional theory, when unsaturated states are not properly passivated, a planar structure is obtained; however, when two layers of planar 2D nitrides come into contact, bonding beyond vdW occurs, leading to a semi-metallic behavior. Alternatively, when unsaturated states are properly passivated (using partially charged pseudo hydrogen), the structure is the most stable in the buckled form.¹⁶ Recently, Vasu *et al.* reported the effect of

vdW pressure of 2D crystals inside the nano-enclosures by investigating the stability of trapped compounds using both Raman spectroscopy and transmission electron microscopy (TEM). They found that vdW assembly of 2D crystals creates huge pressure (as high as 1 GPa) at heterostructure interfaces, leading to unexpected physical and chemical properties of trapped molecules. Vasu *et al.*³ performed TEM analysis of graphene as an archetype 2D crystal for preparing encapsulated MgO molecule/salt structures. They obtained MgO nanocrystals starting from hydrated MgCl₂. Surprisingly, the 125 cm⁻¹ Raman peak observed was previously reported for MgO crystals as a difference Raman band.³ Elemental analysis using energy dispersive X-ray (EDX) spectroscopy shows that the flat graphene-encapsulated regions contain magnesium and oxygen. HRTEM analysis further demonstrated that the flat regions are enclosed with thin (mono to few-layers) nano crystallites with a square periodicity and a lattice constant of 2.1±0.05 Å.³ Although these experiments open up new opportunities for optoelectronic device fabrication, to our knowledge a fundamental understanding of the electronic interaction of these vdW assembly of 2D crystals with graphene layers and their optical absorption have received little attention so far.

In this work, we present the first theoretical study of electronic and optical properties of 2D MgO (square lattice) encapsulated between bilayer graphene (BLG). We carry out a systematic analysis of a single, bi, tri, and four MgO flakes adsorbed on a single layer graphene (GE) and encapsulated between BLG with the help of a variety of first-principles density functional theory (DFT) calculations. We demonstrate and analyze key features of the system such as the stability of adsorption, the associated MgO flake geometry, charge transfer, electronic density of states (DOS), band structures, and vdW pressure between graphene layers. We validate our theoretical results of vdW pressure estimation on BLG with experimental values recently reported [3].

Furthermore, we demonstrate, for the first time, the optical absorption spectrum of single flake MgO and its absorption on GE and encapsulated form of MgO between BLG by using of BerkelyGW (BGW) packages. Interestingly, our results show that while there is one quantum emission in visible light region for single MgO flake, there are wide ranges of visible light regions for MgO@GE and MgO@BLG. These novel electronic and optical properties of MgO flakes can be exploited to modulate materials confined at the atomic interface.

2- Computational methods

Electronic properties of adsorption of MgO flakes on graphene layers were performed with SIESTA software package based on the self-consistent density functional theory (DFT) calculations and periodic supercell method.¹⁷ The calculations were performed within the generalized gradient approximation (GGA) in conjunction with double-zeta polarized orbital for the localized basis sets and a norm-conserving Troullier-Martins type pseudo potential for magnesium, oxygen and carbon. Concerning the role of vdW forces, we compared the DFT results based on GGA and vdW function (vdW-DF)¹⁸ as described by Roman-Perez and Soler.¹⁹ The sampling of the Brillouin zone includes 18×18×1 Monkhorst-Pack k-points grid to produce an accurate band structure for all adsorption cases studied. The geometry optimization was pursued until the convergence criterion was less than 10⁻⁵ eV for total energy and less than 0.01 eV/Å for forces.^{20,21} The normalized clustering energy for (MgO)_n is defined by:

$$\Delta E(n) = E(MgO) - E((MgO)_n)/n \quad (1)$$

where $E(\text{MgO})$ is the total energy for optimized gas-phase MgO, $E(\text{MgO})_n$ is the total energy for optimized MgO nanocluster, n is the number of MgO units and $\Delta E(n)$ is the normalized clustering energy.

Optical properties of MgO flakes and its adsorption on GE and encapsulation between BLG were computed using the BGW package based on first-principles many body perturbation theory.^{22,23,24}

To characterize the electronic excited states of these systems for optical properties, we have employed GW/BSE as implemented in BerkeleyGW package, where the computational steps are given in Figure 1.

The quasi-particle energies are computed using GW approximation, via a first-order correction to DFT eigenvalues, within the generalized gradient approximation and Perdew, Burke, and Ernzerhof with starting DFT-PBE eigenvectors and eigenvalues taken from the SIESTA and Quantum Espresso DFT package, which is compatible with the BGW implementation. The optical excitations have been computed via a Beth-Salpeter equation (BSE) by explicit inclusion of electron-hole interactions. The static dielectric function has been computed within the random-phase approximation, and the frequency dependence of the dielectric function is extended to finite frequency via the generalized Plasmon-pole (GPP) model and optical excitation energies by inclusion of electron-hole interaction from the solution of Bethe-Salpeter equation (BSE).^{22,25} Figure 1 shows a schematic representation of the steps involved in the calculations of dielectric function $\epsilon(\omega)$ and quasiparticle (QP) energies, within the BerkeleyGW approximation.

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 determined via the standard expression:^{24,26}

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

where ω has a unit of energy (in atomic units).

The plane wave energy cutoff for the DFT calculations was 720 eV. To build the dielectric function, the total number of states are 2100, spanning an energy greater than 30 eV. The dielectric function plane wave cutoff is 180 eV. The convergence of exciton wavefunctions and correlation functions for flakes are obtained by using a real space $38 \times 38 \times 20$. The BSE sum was computed using 8 (16) valence $\times$ 8 (16) conduction states for heterostructures of graphene and MgO.

Moreover, we calculated the exciton wavefunction, $\psi(r_e, r_h)$ from the BSE as a linear combination of single excitations from the ground state, where one electron is promoted from an occupied to an unoccupied state, and evaluate its spatial extent and distribution via an electron-hole correlation function, $F(r)$. By definition,²² $F(r)$ is the probability of finding hole and electron separated by a distance $\mathbf{r}$ as:

$$F(r) = \int_{\Omega} d^3r_h |r_e = r_h + r, r_h|^2 \quad (3)$$

where r_e is electron coordinates and r_h is the hole coordinates, and Ω is the volume of a primitive cell.

3- Results and discussion

3.1 Nanoclusters of MgO

Several experimental studies have been done for MgO nanoclusters by using transmission electron microscopy,²⁷ laser ionization time of flight spectroscopy,^{28,29} and tunable IR-UV two-color ionization.³⁰ Moreover, there are a number of theoretical studies on the electronic properties^{31,32,33} of MgO nanoclusters by using ion-pair potential^{34,35,36,37,38,39,40,41,42} and structure stabilities using ab initio and molecular dynamics without global optimization.^{43,44,45} Recently, Chen *et al.*⁴⁶ reported the global minima for (MgO)_n nanostructures using a genetic algorithm in conjunction with MNDO/MNDO/d semi-empirical molecular orbital calculations.⁴⁶ This group showed that the normalized clustering energy for (MgO)_n increases as n increases, where the slope of clustering energy decreases.⁴⁶

Before studying the adsorption of different MgO nanoclusters on GE and between BLG, we carried out a systematic analysis for a primitive interfacial unit cell that simulates global minima (annealing method) structures of isolated square lattice of single-flake (SLF) (MgO)₁₆, bilayer-flake (BLF) (MgO)₃₂, trilayer-flake (TLF) (MgO)₄₈ and fourlayer-flake (FLF) (MgO)₆₄ (Figure 2a-d). For (MgO)_n n=8,16,24,32, the $\Delta E(n)$'s calculated at the GGA exchange correlation by SIESTA. $\Delta E(8) = 5.47 \text{ eV}$, $\Delta E(16) = 6.69 \text{ eV}$, $\Delta E(24) = 6.92 \text{ eV}$, $\Delta E(32) = 7.24 \text{ eV}$. These results reveal that the normalized clustering energy $\Delta E(n)$ for the (MgO)_n increases as n increase, which is in good agreement with Chen *et al.* results.⁴⁶

DFT results are summarized for isolated MgO flakes in Table 1. Figure 2e-h shows the total density of states (DOS) of SLF (e), BLF (f), TLF (g) and FLF MgO (h). The Fermi energy (E_F), indicated by the dashed lines, and the energy difference of HOMO/LUMO (energy gap) are 2.86 eV for SLF, 2.56 eV for BLF, 2.12 eV for TLF and 2.4 eV for FLF. This indicates that band gap closing happens for MgO flakes, and TLF has the least energy gap, likely due to the presence of more symmetry than other flakes. The electrical dipole moment for SLF (-0.58,-0.04,0.05), BLF

(-0.008,0.02,0.01), TLF (-0.002,-0.01,-0.005) and FLF (0.02,0.04,-0.08) reveals that intrinsic electric field for TLF is the least; in other words the inter-particle interactions between neighbours are weak, thus the broken symmetry in regard to the intrinsic electric field for TLF MgO is the least. If we compare the angle between optimized SLF (90° - 100°), BLF (88° - 97°), TLF (92° - 96°) and FLF (92° - 99°), our findings confirm that optimized TLF has more steric symmetry than other configurations. Moreover, the bond length for TLF MgO is 1.92-1.94 Å, while that of other structures are 1.9-1.97 Å.

To obtain a deep understanding of the electronic interaction of MgO flakes adsorbed on graphene substrates, we performed first-principles calculation presented in next sections.

3.2 MgO nanoclusters over GE

Considering that molecular doping of graphene layers can induce gap,^{48,52,53} we may expect a small band-gap for MgO nano clusters on graphene. Here, we study adsorbed MgO nano clusters on graphene to probe the electronic and magnetic properties of these systems. We focus on adsorbed single-, bilayer-, trilayer- and fourlayer-stack MgO/GE (Figure 3). As a first step in the adsorption process, Table 2 shows our DFT results on adsorption energy (E_{ads}), the distance between the mass center of MgO layer and the graphene sheet ($d_{\text{cent-cent}}$), electrical dipole moment p_z , magnetic moment M , the net Mulliken charge on MgO and finally energy gap E_g . In view of Table 2, the following findings deserve attention: (i) 2D SLF MgO is the most stable system among the studied complexes, (ii) the distance $d_{\text{cent-cent}}$ associated with the height of the MgO mass center decreases from SLF to FLF MgO, and (iii) the energy gap form SLF to FLF

MgO increases. In essence, the structural deformation ($d_{\text{cent cent}}$) of the adsorbate is more important for the most stable systems while the charge transfer plays a less pronounced role. Such structural deformations are originated from the minimization of π - π repulsion of delocalized graphene electrons and π -orbital of O, and also from improving electrostatic attractions between O atoms of MgO and C atoms of graphene. The structural deformations essentially decrease in multilayer-stack MgO, since they form directional bonds among MgO units that flattened the MgO layers. The interactions of MgO with graphene become weaker after creation of multilayer MgO but still have a profound influence on the electronic properties of the substrate.

The calculated Mulliken charges (Table 2) manifest that adsorbed MgO is negatively charged, consistent with the electron withdrawing behavior of O species. But graphene is positively charged or p-doped. SLF MgO has the least charge transfer, and the maximum structural deformation and stability among all studied MGO flakes. One plausible explanation is that the structural deformation of MgO facilitates a donation (overlap) between oxygen atoms and graphene, stabilizing the adsorbed single flake MgO. However, the orientation of this deformation decreases the ability of π -orbital of MgO to accommodate additional charges from graphene or does not facilitate any back donation.^{47,48} Figure 4 summarized the influence of structural deformation on the charge transfer between adsorbate and substrate. Nevertheless, we need to emphasize that the inverse mechanism works where the donation is larger for bilayer-, trilayer-flakes that are closer to the graphene surface than the single flake.

Figure 3 shows the electronic band structure and total density of states (spin up and down) (DOS) of MgO flakes on graphene, with respect to the DOS of pristine graphene. The DOS of

graphene are perturbed by adsorption of MgO, because of large adsorption energy and charge transfer between adsorbate and substrate. There is no covalent bonding between the two species, thus one could anticipate that most of the physical properties of graphene will be conserved. As expected, the DOS (flake/graphene) is more or less a direct superposition of DOS(graphene) + DOS(flake). The states of graphene in CB are slightly perturbed due to adsorption of flake, while VB are strongly affected by flake adsorption and because of the existence of O electron-withdrawing MgO, some electrons from the valence band (VB) of graphene are transferred to flake. Hence, the DOS of flake/graphene is shifted by 0.2 eV, which indicates p-doping of graphene, in agreement with Mulliken charge analysis in Table 2.

With careful inspection of DOS of our systems, we notice the existence of peaks or localized states near the E_F , which causes slightly flat band and relatively weak band dispersions near the E_F . The weak dispersion of bands near E_F implies a localization of the states, and confirms the physisorption interaction between MgO moieties and the surface. In this regard, we computed and plotted the electronic band structures of MgO columnar stacks on graphene. Since DFT usually underestimated the band gap,^{49,50} we investigated the electronic properties using the quasiparticle GW approximation to have more accurate energy gaps. Figure 3a indicates that the magnitude of band gap opening for SLF MgO is 36 meV with PBE (94 meV with GW). In the case of BLF MgO/GE (Figure 3e), the magnitude of band gap opening is 40 meV with PBE (115 meV with GW). This band gap opening is 46 meV for TLF MgO/GE with PBE (124 meV with GW) as shown in Figure 3i. Finally in the case of FLF MgO/GE (Figure 3m), the magnitude of band gap openings is 74 meV with PBE (176 meV with GW).

The above calculated band gap openings originate from the charge transfer and states mixing of the adsorbate with graphene by breaking the local symmetry of electronic band states of

graphene. Chang and collaborators^{51,52} reported that the adsorption of different aromatic molecules such as benzene (C_6H_6), triazine ($C_3N_3H_3$) and borazine ($B_3N_3H_6$) on graphene induce a band gap opening up to 63 meV. To explain the origin of band gap opening, they computed a redistribution of charges among the adsorption sites, and concluded that the broken symmetry of band-states of graphene by adsorbate.⁵¹ Our previous works on the adsorption of isolated and self-assembled TMA layer on graphene^{48,53,54} also demonstrated the influence of chemical nature and the geometry of adsorbed molecular networks on the electronic band gap based on scanning tunneling microscopy (STM) and orbital mixing.

Our findings for SLF MgO on graphene show a strong modification of the electronic states (Figure 3b,c) in the energy range within 5.0 eV below the Fermi energy. In fact, both the projected DOS (pDOS) and scanning tunneling microscopy profile (STM) manifest the formation of hybrid interface states. To identify an adsorption mechanism, a pDOS in Figure 3c is presented to probe the modification of HOMO and LUMO after absorption. The resulting scenario allows us to discriminate the single flake/GE interface from a simple physisorption by charge transferring between substrate and adsorbate.

We inspect the electronic properties of the interface by computing pDOS on the eigenstates of the free MgO flake, presented in a small energy window, from -6 to -3 eV in terms of orbitals of the (isolated) molecule. The HOMO, LUMO, and HOMO-1 pDOS for gas-phase single flake are shown in Figure 3c. The shapes of these signals are completely different from the SLF adsorbate on graphene, demonstrating mixing of the electronic states. The HOMO pDOS is split into two main structures (around -5 and -4.2 eV), the LUMO pDOS has double peaks, centered at -3.5 and -3 eV, and the HOMO-1 pDOS is broadened and presents a number of weaker features. To strengthen our analysis of electronic states mixing, we also visualized the STM simulation

images and their profile of the adsorbate system. One example is shown in Figure 5 corresponding to SLF MgO/GE.

To probe the electronic states and states mixing in our system, we obtained the simulated STM images for the adsorption of SLF MgO on GE using numerical STM tool. Figure 5 gives a perspective of the influence of SLF MgO on STM images. This Figure shows the topographic simulated STM images calculated above the SLF MgO. Computing a STM image could reveal subtle information on the variation of electronic properties and extra electronic states; red protrusions are related to negative charge accumulation on MgO moiety, consistent with Mulliken charge analysis presented in Table 2.

Figure 6 gives scanning tunneling microscopy (STM) simulation images to discover the influence of different flakes of MgO/graphene. The upper panels (Figure 6a,b,c,d) presenting the STM simulation images were computed from the bottom of the samples (MgO flakes/GE) where we have simply flipped the MgO/graphene sample upside-down. To analyze those simulation images of flipped samples, the STM profiles contrasts are plotted along two different lines (A, B). This result supports the fact that MgO interacts strongly with the surface, and the main STM contrasts are localized nearby the MgO flakes.

STM profiles convey information on the local density of states (LDOS) of graphene along the lines A and B, which is a regular pattern of corrugation for pristine graphene. The LDOS for MgO/GE complexes reveals a depletion in the region of adsorbate. This depletion appears more pronounced for the four layer-flake, followed by trilayer-, bilayer-flake MgO, which support an improved mixing of states and larger band gap opening. In contrast, the LDOS of a single flake

MgO/GE with the least LDOS depletion reveals more symmetrical feature than other flakes. As a result, the band gap opening for adsorption of single flake/GE is smaller than other structures.

3.3 MgO nanoclusters encapsulated between BLG

As shown in the previous section, the adsorption of MgO flakes on SGL may modify and tune the electronic properties of graphene through molecular deformations on the adsorbate. Such structural deformations can play a major role upon forming 2D and 3D networks between bilayer graphene. In order to validate with the previously reported experimental results,³ and acquire detailed analysis of vdW pressure on trapped MgO flakes between BLG, in this section we focus on the variation of electronic properties induced by MgO layers encapsulated between BLG. We investigated four network structures shown in Figure 7.

We start our discussion with a detailed description of DFT optimized geometries such as bond length and angle (Figure 7c,f,i,l) and adsorption energy (E_{ads}), the distance between the mass center of MgO layer and the graphene sheet ($d_{\text{cent-cent}}$), electrical dipole moment p_z , magnetic moment M , the net Mulliken charge on MgO, energy gap E_g and finally electrostatic pressure between graphene layers (Table 3). In the light of Table 3, we infer the following: (i) TLF MgO is the most stable system with electrical dipole moment (3.32 Debye), followed by SLF MgO, BLF and FLF MgO (ii) the distance $d_{\text{cent-cent}}$ associated with the height of the MgO mass center decreases from SLF flake to FLF MgO, (iii) electrostatic pressure ($P = \frac{\sum_{i,j} F_{i,j}}{A}$, where $F_{i,j}$ is the force on i th atom due to j th atom in BLG and A is the graphene area) is highest (0.72 (0.93) GPa) for SLF, followed by BLF (0.62 (0.81) GPa), TLF (0.65 (0.85) GPa), and FLF (0.46 (0.68) GPa), numbers inside parenthesis are calculated by vdW-DF approaches. In particular, our

calculated pressure for SLF is in close agreement with experimental pressure (1.2 ± 0.3 GPa).³ Interestingly, experimental data³ shows that the trapped MgO@BLG samples contain numerous flat regions with ($h \approx 10\text{\AA}$) which is the distance between graphene layers in our computational model at TLF (the most stable structure) as shown in Figure 7i. This level of consistency between experiments and computations is quite encouraging. One plausible explanation for the most stable flake (TLF@BLG) is that the electrical dipole moment creates intrinsic electric field for TFL@BLG (as added in Table 3) greater than other flakes, thanks to the electric dipole moment along the z axis of system. Electrical dipole moment enhances the inter-particle forces between neighbouring particles. These intermolecular and inter-particle forces cause steric or electrostatic stabilization. Also, in the section 3.1 (nanoclusters of MgO), we found that gas phase of TFL has greater symmetry related to other configurations, which help to have more stability between bilayer graphene.

Figure 7 compares the calculated band structures and DOS of MgO columnar stacks between BLG. In the case of SLF MgO@BLG (Figure 7a,b), the magnitude of band gap opening is 41 meV with PBE (114 meV with GW). This gap opening is 0 meV for BLF MgO@BLG with PBE (48 meV with GW) as illustrated in Figure 7d,e. TLF MgO@BLG has a band gap openings of 21 meV with PBE (81 meV with GW) as shown in Figure 7g,h and finally FLF MgO@BLG has band gap openings of 11 meV with PBE (66 meV with BGW) as shown in Figure 7j,k. Similar to our previous observation in the case of GE, the existence of peaks or localized states near the E_F flattens bands and weakens bands dispersions near the E_F . To summarize, unlike the case of single layer graphene, the most stable system is TLF MgO@BLG where the isolated TLF MgO has less energy gap (Table 1) with high level of symmetry.

Previous DFT studies⁵⁵ on similar systems (BLG and F4-TCNQ) have shown a large band gap opening of 253 meV, due to built-in electric field between graphene layers via the large charge transfer (0.45 |e|) from the top graphene layer to F4-TCNQ, as a strong electron acceptor. Analogously, our own previous DFT study⁵⁶ on electronic properties of adsorption of fluorine molecular (F₂) on GE and between BLG has shown that the broken symmetry of graphene layers induced by the charge transfer between adsorbate and substrate introduces the gap opening. Thus, we suggest that in the case of MgO@BLG, the origin of the gap opening lies in the charge transfer between top and bottom graphene layers, creating built-in electric field between layers, which entail broken inversion symmetry.

4- Optical Properties

The optical properties of Magnesium oxide, MgO nanoparticles, as the simplest of oxides is a subject of several experimental and computational studies.⁵⁷ Cubic nanoparticles of MgO (nanocubes) could absorb light below the band gap of the bulk oxide (7.8 eV); e.g. 3 nm MgO nanocubes^{57,58} absorb at 220 and 270 nm (5.6 and 4.6 eV) compared to 160 nm (7.8 eV) for the bulk.⁵⁹ MgO nanoparticles display luminescence at ~370 nm (~3.6 eV) for the same nanoparticles size (3 nm).^{58,60} The absorption and luminescence spectra of alkaline oxide nanoparticles can be experimentally tuned and controlled by varying the nanoparticle size.⁵⁸

The alkaline oxides such as MgO are wide band gap insulators without quantum confinement behavior, in contrast to small band gap semiconductors. Moreover, these alkaline oxides (for which the light absorption is smaller than bulk band gap) show blue shift with increasing particles size^{57,58,61} rather than the red shift expected from quantum confinements.

4.1 MgO nanocluster

To utilize the solar energy, a photocatalytic material should have wide absorption range of solar energy and band gap around 2-3 eV.⁶² We see in Table 1 that the SLF MgO has a band gap of 3.22 eV and the monolayer MgO has a direct band gap of 4.86 eV smaller than the bulk phase. Although the electronic band gap of monolayer MgO is decreased, it is still too large for practical applications, which needs to be narrowed further for photocatalytic applications.

Figure 8a-b shows the optical absorption spectrum computed for the isolated flake, SLF MgO, for exciton (solid lines) and for the non-interacting electron-hole case (dashed lines), demonstrating a single emission which is located at 1.9 eV in the visible light range (1.64-3.19 eV or 390-760 nm). Figure 8c-d reveals that the computed lowest excitation energy for TLF MgO is located at 2.2 eV followed by 2.7 eV, both in visible light range and the several peaks in UV range. These results are in good agreement with energy gap presented in Table 1 for TLF (2.48 eV), which is the smallest energy gap and the most stable structure between BLG.

Hence, more direct comparison of predicted absorption spectra for the different MgO flakes (Figure 8a,c) with an experimental spectrum of nanoparticles would be beneficial. The absorption spectrum shows blue shift for larger particles.^{57,58,59} The absorption spectrum for TLF (MgO)₄₈ shows blue shift. More specifically, for the SLF (MgO)₁₆ the position of the peak maximum at ~ 1.7-1.9 eV (729-652 nm) shifts to shorter wavelength with increasing particle size, i.e. TLF. The first peak in the spectrum of the TLF displays a blue shift to ~ 2.1-2.2 eV (590-563 nm) and a second strong peak is located in the range of 2.7-2.8 eV (459-442 nm).

To obtain deep insights to the diffusion properties of excitons in 2D and 3D MgO crystals, we analyze the spatial distribution of excitons within the 2D and 3D MgO crystals. Electron and

hole exist everywhere in the crystal due to the periodicity and the symmetries of crystal with correlated relative motion. Here, we use the Equation 3 which is the probability of finding the electron and hole separated by a distance, $\mathbf{r}$, to acquire distribution of a given exciton in terms of relative electron and hole coordinates. As mentioned in computational details, $F(|\mathbf{r}|)$ is the correlation function of (probability of finding) an electron and hole separated by $\mathbf{r}$. Figure 9a,b presents density plot of $F(|\mathbf{r}|)$ for the first excited-states of 2D and 3D MgO, projected onto xy plane. $F(|\mathbf{r}|)$ in 9c-d is the correlation function of electron-hole distance which fits to a Gaussian function.

The origin for both electron and hole is identical such that point $\mathbf{r} = 0$ corresponds to electron and hole occupying identical coordinates. The exciton amplitude decays at long distances as shown in Figure 9c-d, due to attractive Columbic interaction between electron and hole. For the first-excited state of 2D MgO, this function peaks at 0 Å and has a full width half-maximum (fwhm) of 3.1 Å, while for the first-excited state of 3D MgO, it peaks at 5 Å (larger than the average electron-hole distance) and has fwhm of 4.3 Å. These results reveal that exciton correlation and electron-hole interaction for the first excited state at 2D MgO is weaker and more localized than 3D MgO, leading to single quantum emission at visible range.

4.2 MgO nanocluster on GE

2D materials such as graphene attract significant attentions for photodetection due to unique optical properties, such as high carrier mobility and strong interaction with photons.⁶³ However, the metallic nature of graphene (gapless) prevents its use as light emitting device in optoelectronic devices. Combining different 2D materials with different lattice constant construct heterostructures, leveraging nanophotonic properties and its applications. Britnell *et*

*al.*⁶⁴ showed that if a tungsten disulfide (WS_2) layer is sandwiched within two graphene layers, this heterostructure will form an efficient, “Schottky diode like” solar cell.⁶⁴ In this device, graphene acts as a transparent electrode to collect photo-generated carriers, and the WS_2 semiconductor works as the active energy harvesting material.⁶⁴ Analogously, the integration of graphene and MgO to form heterostructures could tune the optical properties of metallic graphene for optoelectronic applications. As shown in Figure 3a-d (section 3.2), the optimized geometries of different MgO stacks on graphene layer can create energy gap for graphene due to symmetry breaking. Therefore, the tunable electronic band gap of graphene by molecular adsorption makes it suitable for optoelectronic applications. Figure 8e compares the optical absorption spectrum computed for the MgO flake on graphene layer in two different phases; for exciton (solid line) and for non-interacting electron-hole case (dashed line). Absorption spectrum for MgO/GE is wide because of small energy gap for MgO/GE (Table 2). The absorption spectrum covers visible light range (1.5-3.5 eV) for this system. The value of GW gap from Figure 8f is around 1eV, which is relevant for a wide range of absorption spectra for MgO/GE (Figure 8e). In the next section, we perform similar GW calculations to get the optical absorption behavior of SLF MgO encapsulated between bilayer graphene.

4.3 MgO nanocluster encapsulated between BLG

Given that molecular doping of graphene layers can induce gap,^{48,52,53} MgO flake@BLG systems can make BLG suitable for several optoelectronic nanodevices (Figure 7a-d, section 3.3). Figure 8g compares the optical absorption spectrum computed for the MgO flake between bilayer graphene in two different phases; for exciton (solid line) and for non-interacting electron-hole case (dashed line). Absorption spectrum of MgO/GE is wider than MgO@BLG, because of smaller energy gap of MgO/GE. The absorption spectrum covers visible light range

for both systems. We find that the GW gap of MgO@BLG (Figure 8h) is around 2 eV greater than that of MgO/GE system. These optical properties indicate the importance of vdW crystals, especially 2D MgO flakes, in nanooptoelectronic applications. Our DFT results for optical properties of heterostructures of graphene and MgO suggest that integration of 2D materials enhances light-matter interactions, which offers the novel discovery in nanophotonic devices and graphene detectors for a wide range of electromagnetic spectra.

5. Conclusion

We studied the electronic and optical properties of MgO nanoclusters and their adsorptions and encapsulation on GE and BLG, respectively.⁵⁶ Our results demonstrate that extremely large pressures are exerted on MgO nanoclusters between BLG - in close agreement with experiments³ – which can modulate physical and chemical properties of vdW heterostructures. We found that the magnitude of the p-type doping and band gap opening strongly depend on the structural deformation in GE while the vdW pressure of graphene layers and polarization of top and bottom layers dominate the gap opening in BLG. These structural deformations and statistical pressure decrease in the double-, tri- and four-layer of MgO flake, where the Mg and O atoms form directional bonds among units. Since we are comparing the stability of the different conformations in terms of relative energy, charge transfer, structural deformation, and energy gap, the larger size of flakes will create a layered network on graphene, which improves the stability of the layer but its adhesion on graphene is significantly lowered. It is also interesting to investigate these heterostructures for large sizes of flakes. Our previous works^{48,52} show that the layered network added on graphene could tune the electronic properties of graphene; for example the magnitude of band gap opening appears to be strongly correlated

with breaking the symmetry of π -states of graphene while the magnitude of p-doping in graphene per adsorbate unit remains nearly constant for the added network layers.⁴⁸

Using the BGW package, we showed that SLF MgO includes one quantum emission and TLF has two peaks in the visible light region but interestingly a wide range of visible light is accessible for MgO/GE and MgO@BLG. This work highlights the merit of vdW heterostructures in trapping MgO flakes between BLG and manifest interesting electronic and optical properties, which can play a major role in modulating the performance of optoelectronic devices such as nano-transistors and solar cells. In view of the remarkable defect and edge effects of graphene, activated graphene with both exposed free and bound edges offer more active sites and could dramatically alter their electronic and optical properties.⁶⁵ Also, localized defects in hexagonal boron nitride and in functionalized BN cause single-photon emission at room temperature, which has applications in bio-imaging and biosensing.^{66,67} Overall, the methods and strategies of this work can have implications on fabricating several new hybrid 2D and 3D heterostructures and hybrid materials through encapsulating external molecules.⁶⁸⁻⁷⁶

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Author Contributions

F.S. and R.S. designed the research; F.S., J.B., M.N.A. performed the computational research and F.S. and R.S. analyzed the data; and F.S. and R.S. wrote the paper.

Competing Financial Interest

The authors declare no competing financial interest.

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Table 1. DFT results for different MgO, bond length of MgO flakes, electrical dipole moment p_z , magnetic moment M , the net Mulliken charge on MgO, energy gap E_g

MgO	bulk	monolayer	16	32	48	64
$d_{\text{Mg-O}}(\text{\AA})$	2.02	1.95	2	2.03	2.06	2.04
p (Debye)	0	0	(-0.58,0.04,0.05)	(0.008,0.02,0.01)	(0.002,-0.01,0.005)	(0.02,0.04,-0.08)
M (μ_B)	0	0	0	0	0	0
E_g (eV)	6.1	3.78	2.86	2.56	2.12	2.4
E_g (eV)BGW	7.3	4.86	3.22	2.98	2.48	2.77

Table 2. Structural analysis of optimized adsorbed MgO nanoclusters on Graphene., adsorption energy (E_{ads}), the distance between the mass center of MgO layer and the graphene sheet ($d_{\text{cent-cent}}$), electrical dipole moment p_z , magnetic moment M , the net Mulliken charge on MgO, energy gap E_g

(MgO) _n /GE	16	32	48	64
E_{ads} (eV)	-2.99	-2.28	-2.35	-1.79
$d_{\text{cent-cent}}(\text{\AA})$	3.36	3.09	3.05	3.12

p_z (Debye)	-0.91	-1.46	0.04	0.34
M (μ_B)	0.57	0.13	0.15	0.24
MgO net charge ($ e $)	-0.1	-0.22	-.2	-0.13
E_g (meV)	36	40	46	74
E_g (meV) BGW	94	115	124	176

Table 3. Structural Analysis of Optimized Adsorbed MgO Layers between Bilayer Graphene (BLG), adsorption energy (E_{ads}), the distance between the mass center of MgO layer and the graphene sheet ($d_{cent-cent}$), electrical dipole moment p_z , magnetic moment M , the net Mulliken charge on MgO, energy gap E_g and electrostatic pressure P . The numbers inside parenthesis are calculated by vdW-DF.

$(MgO)_n@BLG$	16	32	48	64
E_{ads} (eV)	-4.91(-5.27)	-4.4(-4.81)	-5.05(5.41)	-4.15(-4.53)
$d_{cent-cent}(\text{\AA})$	3.2	3.1	3.0	3.06
p_z (Debye)	-0.61	0.21	3.23	1.76
M (μ_B)	0.68	0.0	0.13	0.11
MgO net charge ($ e $)	-0.3	-0.47	-0.34	-0.41
E_g (meV)	41	0	21	11
E_g (meV) BGW	114	48	81	66
Pressure(GPa)	0.72 (0.93)	0.62 (0.81)	0.65 (0.85)	0.46 (0.68)

Figure 1. Schematic representation of the steps involved in the calculations of dielectric function $\epsilon(\omega)$ and quasiparticle (QP) energies, within the BerkeleyGW approximation. The Kohn-Sham energies and occupied and unoccupied orbitals ϕ computed at the DFT level are input to the GW and Bethe-Salpeter equation (BSE), which is used to the dielectric matrix and absorption function.

Figure 2. DFT optimized structures of (a) single-flake, (b) bilayer-flake, (c) trilayer-flake and (d) fourlayer-flake MgO. Total density of states (DOS) of (e) SFL, (f) BLF, (g) TLF and (h) FLF MgO. The Fermi energy (E_F) indicated by the dashed line and the energy difference of HOMO/LUMO (gap energy) of gas phase are 2.86 eV for (a) 2.56 eV for (b) 2.12 eV for (c) and 2.4 eV for (d).

Figure 3. Electronic band structures and total density of states for adsorption of MgO columnar stacks on single layer graphene. (a) single-flake MgO/GE, the magnitudes of band gap opening is 36 meV with PBE (94 meV with BGW), and (b) shows the comparison of DOS for spin up and down and the pristine GE, (c) pDOS for free SLF and adsorbate on graphene, (e,f,g,h) bilayer-flake MgO/GE, the magnitude of band gap openings is 40 meV with PBE (115 meV with BGW), (i,j,k,l) trilayer-flake MgO/GE, the magnitude of band gap openings is 46 meV with PBE (124 meV with BGW), (m,n,o,p) fourlayer-flake MgO/GE, the magnitude of band gap openings is 74 meV with PBE (176 meV with BGW).

Figure 4. Influence of structural deformation on the charge transfer mechanism (donation and back-donation) between single-flake and bilayer-flake MgO and graphene.

Figure5. STM simulation images of adsorption of single-flake MgO on graphene, which red color show negative charge accumulation on substrate. STM images were calculated with $I = 0.1$ nA and $V_b = -0.5$ V.

Figure 6. Simulated STM images from bottom and STM profiles along lines A and B for (a) single-flake, (b) bilayer-flake, (c) trilayer-flake and (d) fourlayer-flake MgO on graphene, compared to pristine. STM images were calculated with $I = 0.1$ nA and $V_b = -0.5$ V.

Figure 7. Electronic band structures and total density of states for adsorption of MgO columnar stacks between bilayer graphene. (a) single-flake MgO@BLG, the magnitudes of band gap opening is 41 meV with PBE (114 meV with BGW), and (b,c) shows the comparison of DOS for spin up and down and the pristine GE, (d,e,f) bilayer-flake MgO@BLG, the magnitude of band gap openings is 0 meV with PBE (48 meV with BGW), (g,h,i) trilayer-flake MgO@BLG, the magnitude of band gap openings is 21 meV with PBE (81 meV with BGW), (j,k,l) fourlayer-flake MgO/GE, the magnitude of band gap openings is 11 meV with PBE (66 meV with BGW).

Figure 8. Comparison of the optical absorption spectrum computed for (a) 2D isolated MgO flake, (c) TFL MgO, (e) MgO/GE and (g) MgO@BLG in two different phases; for exciton (solid line) and for non-interaction electron-hole case (dashed line), showing 3 distinct peaks in the absorption spectrum labeled 1-3 for both cases. (b,d,f,h) Joint density of states for exciton; JDOS (solid line) and DOS for non-interaction electron-hole (dashed line).

Figure 9. The two-dimensional electron-hole correlation function, $\mathbf{F}(\mathbf{r})$, for the 2D SLF (a) and 3D TLF (b), projected onto $\mathbf{xy}$ plane, (c),(d) radial distribution of correlation function.