Electro- and opto-mutable properties of MgO nanoclusters adsorbed on mono- and double-layer graphene

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Inspired by recent experiments, the trapping of molecules in 2D materials has gained increasing attention due to the unique ability of the molecules to modulate the electronic and optical properties of 2D materials, which calls 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 a van der Waals pressure of ∼0.7 (0.9) GPa on bilayer graphene encapsulating MgO nanoclusters, which matches extremely well with experiment. While there is one quantum emission in the visible light region for a 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 2D materials with trapped molecules (heterostructures) have gained intense attention because of 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 is an ideal medium for long distance spin transport.4–9 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 nanocluster and thin film perspectives, metal–oxide thin films such as MgO display a 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 resistances of MgO/Co electrodes.5 Dalai et al. fabricated MgO-based double barrier magnetic tunnel junctions for synthesizing CoFeB/Ru/CoFeB free layers to show 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 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 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 type of 2D material. 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 gaps 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. Recently, Vasu et al. reported the effect of the 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. 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 different Raman band. 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) nanocrystallites with a square periodicity and a lattice constant of 2.1 ± 0.05 Å. Although these experiments provide new opportunities for optoelectronic device fabrication, to our knowledge a fundamental understanding of the electronic interaction of these vDW assembled 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 the electronic and optical properties of 2D MgO (square lattice) encapsulated between bilayer graphene (BLG). We carry out a systematic analysis of single-, bi-, tri-, and four-layer MgO flakes adsorbed on 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 (DOSs), band structures, and vdW pressure between graphene layers. We validate our theoretical results of vdW pressure estimation on BLG with experimental values recently reported. Furthermore, we demonstrate, for the first time, the optical absorption spectrum of a single-layer-MgO flake and its absorption on GE and the encapsulated form of MgO between BLG by using BerkeleyGW (BGW) packages. Interestingly, our results show that while there is one quantum emission in the visible light region for a single-layer-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 when confined at the atomic interface.

2 Computational methods

The electronic properties of the MgO flakes adsorbed on graphene layers were investigated with the SIESTA software package based on the self-consistent density functional theory (DFT) calculations and periodic supercell method. The calculations were performed within the generalized gradient approximation (GGA) in conjunction with the double-zeta polarized orbital for the localized basis sets and a norm-conserving Troullier–Martins type pseudopotential for magnesium, oxygen and carbon. Concerning the role of vDW forces, we compared the DFT results based on GGA and vDW function (vdW-DF) as described by Roman-Perez and Soler. The sampling of the Brillouin zone includes a 18 × 18 × 1 Monkhorst-Pack k-point 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⁻¹ for forces. The normalized clustering energy for (MgO)ₙ is defined by:

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

where E(MgO) is the total energy for the optimized gas-phase MgO, E(MgO)ₙ is the total energy for the optimized MgO nano-clusters, n is the number of MgO units and ΔE(n) is the normalized clustering energy.

The optical properties of the MgO flakes adsorbed on GE and encapsulated between BLG were computed using the BGW package based on first-principles many body perturbation theory. To characterize the electronic excited states of these systems for optical properties, we have employed GW/BSE as implemented in the BerkeleyGW package, where the computational steps are given in Fig. 1. The quasiparticle 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 Bethe–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 the electron–hole interaction from the solution of the Bethe–Salpeter equation (BSE).

Fig. 1 shows
a schematic representation of the steps involved in the calculations of the dielectric function $\varepsilon(\omega)$ 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, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The absorption coefficient, $\alpha(\omega)$, is determined via the standard expression:

$$\alpha(\omega) = 2\omega\sqrt{1/2[-\varepsilon_1(\omega) + \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}}],$$

where $\omega$ is the 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 is 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 is obtained by using a real space of $38 \times 38 \times 20$. The BSE sum was computed using 8 (16) valence × 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 evaluated its spatial extent and distribution via an electron–hole correlation function, $F(r)$. By definition, $F(r)$ is the probability of finding holes and electrons separated by a distance $r$ as follows:

$$F(r) = \int_{\Omega} d\mathbf{n}_e |r_e - r_h + r, \mathbf{n}_h|^2,$$

where $r_e$ is the electron coordinate, $r_h$ is the hole coordinate, and $\Omega$ is the volume of a primitive cell.

### 3 Results and discussion

#### 3.1 Nanoclusters of MgO

Several experimental studies have been carried out for MgO nanoclusters by using transmission electron microscopy, laser ionization time of flight spectroscopy, and tunable IR-UV two-color ionization. Moreover, there are a number of theoretical studies on the electronic properties of MgO nanoclusters by using pair potential and structure stabilities using ab initio and molecular dynamics with global optimization. Recently, Chen et al. reported the global minima for (MgO)$_n$ nanostructures using a genetic algorithm in conjunction with MNDO/MNDO/d semi-empirical molecular orbital calculations. This group showed that the normalized clustering energy for (MgO)$_n$ increases as $n$ increases, while the slope of clustering energy decreases.

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 lattices of single-layer-flake (SLF) [MgO]$_{16}$, bilayer-flake (BLF) [MgO]$_{32}$, trilayer-flake (TLF) [MgO]$_{48}$ and fourlayer-flake (FLF) [MgO]$_{64}$ (Fig. 2a–d). For (MgO)$_n$, $n = 8, 16, 24$, and 32, the $\Delta E(n)$ calculated at the GGA exchange correlation by SIESTA are $\Delta E(8) = 5.47$ eV, $\Delta E(16) = 6.69$ eV, $\Delta E(24) = 6.92$ eV, and $\Delta E(32) = 7.24$ eV. These results reveal that the normalized clus-
tering energy $\Delta E(n)$ for $(\text{MgO})_n$ increases as $n$ increases, which is in good agreement with the results of Chen et al.\textsuperscript{46}

The DFT results are summarized for isolated MgO flakes in Table 1. Fig. 2e–h show the total density of states (DOS) of SLF (e), BLF (f), TLF (g) and FLF (h) MgO. The Fermi energy ($E_F$), indicated by the dashed line, and the energy differences of the HOMO/LUMO (gap energy) 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 smallest 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 the intrinsic electric field for TLF is the smallest; in other words the inter-particle interactions between neighbours are weak, thus the broken symmetry with regard to the intrinsic electric field for TLF MgO is the least. If we compare the angle between the optimized SLF (90°–100°), BLF (88°–97°), TLF (92°–96°) and FLF (92°–99°), our findings confirm that the 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 is 1.9–1.97 Å.

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

### 3.2 MgO nanoclusters over GE

Considering that molecular doping of graphene layers can induce gaps,\textsuperscript{48,52,53} we may expect a small band-gap for MgO nanoclusters on graphene. Here, we study adsorbed MgO nanoclusters on graphene to probe the electronic and magnetic properties of these systems. We focus on adsorbed single-layer-, bilayer-, trilayer- and fourlayer-stack MgO/GE (Fig. 3). As a first step in the adsorption process, Table 2 shows our DFT results on the adsorption energy ($E_{\text{ads}}$), the distance between the mass center of the MgO layer and the graphene sheet ($d_{\text{cent}}$), electrical dipole moment $p_z$, magnetic moment $M$, the net Mulliken charge on MgO and finally energy gap $E_g$. As shown in Table 2, the following findings deserve attention: (i) 2D SLF MgO is the most stable system among the studied complexes, (ii) the distance $d_{\text{cent}}$ associated with the height of the MgO mass center decreases from SLF to FLF MgO, and (iii) the energy gap from SLF to FLF MgO increases. In essence, the structural deformation ($d_{\text{cent}}$) of the adsorbate is more important for the most stable systems while the charge transfer plays a less pronounced role. Such structural deformations originated from the minimization of the $\pi-\pi$ repulsion of delocalized graphene electrons and the $\pi$-orbital of O, and also from the improving electrostatic attrac-

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

<table>
<thead>
<tr>
<th>MgO</th>
<th>Bulk</th>
<th>Monolayer</th>
<th>16</th>
<th>32</th>
<th>48</th>
<th>64</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{\text{Mg-O}}$ (Å)</td>
<td>2.02</td>
<td>1.95</td>
<td>2</td>
<td>2.03</td>
<td>2.06</td>
<td>2.04</td>
</tr>
<tr>
<td>$p$ (Debye)</td>
<td>0</td>
<td>0</td>
<td>(−0.58, 0.04, 0.05)</td>
<td>(0.008, 0.02, 0.01)</td>
<td>(0.002, −0.01, 0.005)</td>
<td>(0.02, 0.04, −0.08)</td>
</tr>
<tr>
<td>$M$ ($\mu_B$)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$E_g$ (eV)</td>
<td>6.1</td>
<td>3.78</td>
<td>2.86</td>
<td>2.56</td>
<td>2.12</td>
<td>2.4</td>
</tr>
<tr>
<td>$E_g$ (eV) BGW</td>
<td>7.3</td>
<td>4.86</td>
<td>3.22</td>
<td>2.98</td>
<td>2.48</td>
<td>2.77</td>
</tr>
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</table>
The interactions 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 flatten the MgO layers. The interactions of MgO with graphene become weaker after the 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-layer-flake MgO. However, the orientation of this deformation decreases the ability of the π-orbital of MgO to accommodate additional charges from graphene or it does

**Fig. 3** Electronic band structures and total density of states for adsorption of MgO columnar stacks on single layer graphene. (a) For single-layer-flake MgO/GE, the magnitude of the band gap opening is 36 meV with PBE (94 meV with BGW), and (b) shows the comparison of the DOS for spin up and down and the pristine GE, (c) pDOS for free SLF and the adsorbate on graphene, (e–h) for bilayer-flake MgO/GE, the magnitude of band gap openings is 40 meV with PBE (115 meV with BGW), (i–l) for trilayer-flake MgO/GE, the magnitude of band gap openings is 46 meV with PBE (124 meV with BGW), (m–p) for fourlayer-flake MgO/GE, the magnitude of band gap openings is 74 meV with PBE (176 meV with BGW).
Table 2  Structural analysis of the optimized adsorbed MgO nano-clusters on graphene, adsorption energy ($E_{\text{ads}})$, the distance between the mass center of the MgO layer and the graphene sheet ($d_{\text{cent-cent}}$), electrical dipole moment $p_d$, magnetic moment $M$, the net Mulliken charge on MgO, and energy gap $E_g$

<table>
<thead>
<tr>
<th>(MgO)$_n$/GE</th>
<th>$E_{\text{ads}}$ (eV)</th>
<th>$d_{\text{cent-cent}}$ (Å)</th>
<th>$p_d$ (Debye)</th>
<th>$M$ (μμ)</th>
<th>$E_g$ (meV)</th>
<th>$E_g$ (meV) BGW</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLF</td>
<td>16</td>
<td>32</td>
<td>48</td>
<td>64</td>
<td>94</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>$-2.99$</td>
<td>$-2.28$</td>
<td>$-2.35$</td>
<td>$-1.79$</td>
<td>$36$</td>
<td>$40$</td>
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<tr>
<td></td>
<td>$3.36$</td>
<td>$3.09$</td>
<td>$3.05$</td>
<td>$3.12$</td>
<td>$40$</td>
<td>$46$</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TLF</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>$-0.91$</td>
<td>$-1.46$</td>
<td>$0.04$</td>
<td>$0.34$</td>
<td>$57$</td>
<td>$61$</td>
</tr>
<tr>
<td></td>
<td>$0.57$</td>
<td>$0.13$</td>
<td>$0.15$</td>
<td>$0.24$</td>
<td>$58$</td>
<td>$62$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BLF</td>
<td>115</td>
<td>124</td>
<td>176</td>
<td></td>
<td></td>
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</table>

With careful inspection of the 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, we investigated the electronic properties using the quasiparticle GW approximation to have more accurate energy gaps. Fig. 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 (Fig. 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 Fig. 3i. Finally in the case of FLF MgO/GE (Fig. 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 mixing of states of the adsorbate with graphene by breaking the local symmetry of electronic band states of graphene. Chang and collaborators 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 induces 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 the band-states of graphene is induced by the adsorbate.

Our previous work on the adsorption of isolated and self-assembled TMA layers on graphene also demonstrated the influence of the 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 (Fig. 3b and c) in the energy range within 5.0 eV below the Fermi energy. In fact, both the projected DOS (pDOS) and scanning tunneling microscopy (STM) profile manifest the formation of hybrid interface states. To identify an adsorption mechanism, a pDOS in Fig. 3c is presented to probe the modification of the HOMO and LUMO after adsorption. The resulting scenario allows us to discriminate the single-layer-flake/GE interface from a simple physisorption by charge transfer between the substrate and adsorbate.

We investigated 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-layer-flakes are shown in Fig. 3c. The shapes of these signals are completely different from the SLF adsorbed on graphene, demonstrating the 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 Fig. 5 corresponding to SLF MgO/GE.

To probe the mixing of electronic states and states in our system, we obtained simulated STM images for the adsorption of SLF MgO on GE using a numerical STM tool. Fig. 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 an 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 the MgO moiety, consistent with Mulliken charge analysis presented in Table 2.

Fig. 6 shows scanning tunneling microscopy (STM) simulation images to discover the influence of different flakes of MgO/graphene. The upper panels (Fig. 6a–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 these simulation images of flipped samples, the STM profile contrasts are plotted along two different lines (A and B). This result supports the fact that MgO interacts strongly with the surface, and the main STM contrasts are localized nearby the MgO flakes.

The STM profiles convey information on the local density of states (LDOSs) 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 the adsorbate. This depletion appears more pronounced for the four-layer-flake, followed by trilayer- and bilayer-flake MgO, which supports an improved mixing of states and larger band gap opening. In contrast, the LDOS of a single-layer-flake MgO/GE with the least LDOS depletion reveals a more symmetrical feature than other flakes. As a result, the band gap opening for the adsorption of single-layer-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 in 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 as shown in Fig. 7.

We start our discussion with a detailed description of DFT optimized geometries such as bond length and angle (Fig. 7c, f, i and l) and adsorption energy ($E_{\text{ads}}$), the distance between the mass center of the 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). As seen in Table 3, we infer the following: (i) TLF MgO is the most stable system with an 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 the SLF flake to FLF MgO, and (iii) electrostatic pressure ($P = \frac{\sum F_{ij}}{A}$, where $F_{ij}$ is the force on the $i$th atom due to the $j$th atom in BLG and $A$ is the graphene area) is the 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), and numbers inside parentheses are calculated by vdW-DF approaches. In particular, our calculated pressure for SLF is in close agreement with the experimental pressure (1.2 ± 0.3 GPa).3 Interestingly, experimental data3 show that the trapped MgO@BLG samples contain numerous flat

Fig. 7 Electronic band structures and total density of states for adsorption of MgO columnar stacks between bilayer graphene. (a) For single-layer-flake MgO@BLG, the magnitude of the band gap opening is 41 meV with PBE (114 meV with BGW), and (b and c) shows the comparison of the DOS for spin up and down and the pristine GE, (d–f) for bilayer-flake MgO@BLG, the magnitude of band gap openings is 0 meV with PBE (48 meV with BGW), (g–i) for trilayer-flake MgO@BLG, the magnitude of band gap openings is 21 meV with PBE (81 meV with BGW), (j–l) for fourlayer-flake MgO/GE, the magnitude of band gap openings is 11 meV with PBE (66 meV with BGW).
regions with \( h \approx 10 \, \text{Å} \) which is the distance between graphene layers in our computational model at TLF (the most stable structure) as shown in Fig. 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 an intrinsic electric field for TLF@BLG (as added in Table 3) greater than other flakes, thanks to the dipole electric moment along the \( z \) axis of the system. The electrical dipole moment enhances the inter-particle forces between neighbouring particles. These intermolecular and inter-particle forces cause steric or electrostatic stabilization. Also, in section 3.1 (nano-clusters of MgO), we find that the gas phase of TFL has a greater symmetry related to other configurations, which help to have more stability between bilayer graphene.

Fig. 7 compares the calculated band structures and DOS of MgO columnar stacks between BLG. In the case of SLF MgO@BLG (Fig. 7a and 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 Fig. 7d and e. TLF MgO@BLG has a band gap opening of 21 meV with PBE (81 meV with GW) as shown in Fig. 7g and h and finally FLF MgO@BLG has band gap openings of 11 meV with PBE (66 meV with BGW) as shown in Fig. 7j and 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 band 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 a low energy gap (Table 1) with a high level of symmetry.

Previous DFT studies\(^5\) on similar systems (BLG and F4-TNCQ) have shown a large band gap opening of 253 meV, due to a built-in electric field between graphene layers via the large charge transfer (0.45|e]) from the top graphene layer to F4-TNCQ, as a strong electron acceptor. Analogously, our own previous DFT study\(^6\) on the electronic properties of the adsorption of fluorine molecules (\( E_F \)) on GE and between BLG has shown that the broken symmetry of graphene layers induced by the charge transfer between the 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 a 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.\(^5\) 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\(^5\) absorb at 220 and 270 nm (5.6 and 4.6 eV) compared to 160 nm (7.8 eV) for the bulk.\(^5\) MgO nanoparticles display luminescence at ~370 nm (~3.6 eV) for the same nanoparticle size (3 nm).\(^5\) The absorption and luminescence spectra of alkaline oxide nanoparticles can be experimentally tuned and controlled by varying the nanoparticle size\(^5\) rather than the red shift expected from quantum confinements.

#### 4.1 MgO nanocluster

To utilize the solar energy, a photocatalytic material should have a wide absorption range of solar energy and a band gap around 2–3 eV.\(^6\) 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.

Fig. 8a and b show the optical absorption spectrum computed for the isolated flake, SLF MgO, for excitons (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). Fig. 8c and d reveal that the computed lowest excitation energy for TLF MgO is located at 2.2 eV followed by 2.7 eV, both in the visible light range and several peaks in the UV range. These results are in good agreement with the 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, a more direct comparison of the predicted absorption spectra for the different MgO flakes (Fig. 8a and c) with an experimental spectrum of nanoparticles would be beneficial. The absorption spectrum shows a blue shift for larger particles.\(^5\) The absorption spectrum for TLF (MgO)\(_{16}\) shows a blue shift. More specifically, for the SLF (MgO)\(_{16}\), the position of the peak maximum at \( \sim 1.7–1.9 \) eV (729–652 nm) shifts to a shorter wavelength with increasing particle size, i.e. TLF. The first peak in the spectrum of the TLF displays a blue shift to

### Table 3 Structural analysis of the optimized adsorbed MgO layers between bilayer graphene (BLG), adsorption energy (\( E_{\text{ads}} \)), the distance between the mass center of the MgO layer and the graphene sheet (\( d_{\text{cent-cent}} \)), electrical dipole moment \( \rho_e \), magnetic moment \( M \), the net Mulliken charge on MgO, energy gap \( E_g \) and electrostatic pressure \( P \).

<table>
<thead>
<tr>
<th>(MgO)@BLG</th>
<th>16</th>
<th>32</th>
<th>48</th>
<th>64</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{\text{ads}} ) (eV)</td>
<td>-4.91(-5.27)</td>
<td>-4.4(-4.81)</td>
<td>-5.05(5.41)</td>
<td>-4.15(-4.53)</td>
</tr>
<tr>
<td>( d_{\text{cent-cent}} ) (Å)</td>
<td>3.2</td>
<td>3.1</td>
<td>3.0</td>
<td>3.06</td>
</tr>
<tr>
<td>( \rho_e ) (Debye)</td>
<td>-0.61</td>
<td>0.21</td>
<td>3.23</td>
<td>1.76</td>
</tr>
<tr>
<td>( M ) (μ)</td>
<td>0.68</td>
<td>0.0</td>
<td>0.13</td>
<td>0.11</td>
</tr>
<tr>
<td>MgO net</td>
<td>-0.3</td>
<td>-0.47</td>
<td>-0.34</td>
<td>-0.41</td>
</tr>
<tr>
<td>charge (μ)</td>
<td>-4.15(-4.53)</td>
<td>-4.15(-4.53)</td>
<td>-4.15(-4.53)</td>
<td>-4.15(-4.53)</td>
</tr>
<tr>
<td>( E_g ) (meV)</td>
<td>41</td>
<td>0</td>
<td>21</td>
<td>11</td>
</tr>
<tr>
<td>( E_g ) (meV) BGW</td>
<td>114</td>
<td>48</td>
<td>81</td>
<td>66</td>
</tr>
<tr>
<td>Pressure (GPa)</td>
<td>0.72 (0.93)</td>
<td>0.62 (0.81)</td>
<td>0.65 (0.85)</td>
<td>0.46 (0.68)</td>
</tr>
</tbody>
</table>
Fig. 8 Comparison of the optical absorption spectrum computed for (a) 2D isolated MgO flakes, (c) TFL MgO, (e) MgO/GE and (g) MgO@BLG in two different phases; for excitons (solid line) and for the non-interaction electron–hole case (dashed line), showing 3 distinct peaks in the absorption spectrum labeled 1–3 for both cases. (b, d, f, and h) Joint density of states for excitons; JDOS (solid line) and DOS for non-interaction electron–hole (dashed line).
~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 into 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. Electrons and holes exist everywhere in the crystal due to the periodicity and the symmetries of crystals with correlated relative motion. Here, we use eqn (3) which is the probability of finding the electron and hole separated by a distance, \( r \), to acquire the distribution of a given exciton in terms of relative electron and hole coordinates. As mentioned in computational details, \( F(|r|) \) is the correlation function of (probability of finding) an electron and hole separated by \( r \). Fig. 9a and b present the density plot of \( F(|r|) \) for the first excited-states of 2D and 3D MgO, projected onto the \( xy \) plane. \( F(|r|) \) in Fig. 9c and d is the correlation function of the electron–hole distance which fits to a Gaussian function.

The origin of both electrons and holes is identical such that the point \( r = 0 \) corresponds to electrons and holes occupying identical coordinates. The exciton amplitude decays at long distances as shown in Fig. 9c and d, due to an attractive Columbic interaction between electrons and holes. For the first-excited state of 2D MgO, this function peaks at 0 Å and has a full width at 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 a fwhm of 4.3 Å. These results reveal that the exciton correlation and electron–hole interaction for the first excited state at 2D MgO are weaker and more localized than 3D MgO, leading to single quantum emission in the visible range.

4.2 MgO nanoclusters on GE

2D materials, such as graphene, have attracted significant attention for photodetection due to their unique optical properties, such as high carrier mobility and strong interaction with photons. However, the metallic nature of graphene (gapless) prevents its use as a light emitting device in optoelectronic devices. Combining different 2D materials with different lattice constants to construct heterostructures leverages their nano-photonic properties and applications. Britnell et al. showed that if a tungsten disulfide (WS\(_2\)) layer is sandwiched between two graphene layers, this heterostructure will form an efficient, “Schottky diode like” solar cell. In this device, graphene acts as a transparent electrode to collect photo-generated carriers, and the WS\(_2\) semiconductor works as an active energy harvesting material. Analogously, the integration of graphene and MgO to form heterostructures could tune the optical properties of metallic graphene for optoelectronic applications. As shown in Fig. 3a–d (section 3.2), the optimized geometries of different MgO stacks on the graphene layer can create energy gaps for graphene due to symmetry breaking. Therefore, the tunable electronic band gap of graphene by molecular adsorption makes it suitable for optoelectronic applications. Fig. 8e compares the optical absorption spectrum computed for the MgO flake on the graphene layer in two different phases; for excitons (solid line) and for the non-interacting electron–hole case (dashed line). The absorption spectrum for MgO/GE is wide because of the small energy gap for MgO/GE (Table 2). The absorption spectrum covers the visible light range (1.5–3.5 eV) for this system. The value of the GW gap in Fig. 8f is around 1 eV, which is relevant for a wide range of absorption spectra for MgO/GE (Fig. 8e). In the next section, we perform similar GW calculations to obtain the optical absorption behavior of SLF MgO encapsulated between bilayer graphene.

4.3 MgO nanoclusters encapsulated between BLG

Given that molecular doping of graphene layers can induce gaps, MgO flake@BLG systems can make BLG suitable for several optoelectronic nanodevices (Fig. 7a–d, section 3.3). Fig. 8g compares the optical absorption spectrum computed
for the MgO flake between bilayer graphene in two different phases; for excitons (solid line) and for the non-interacting electron–hole case (dashed line). The absorption spectrum of MgO/GE is wider than MgO@BLG, because of the smaller energy gap of MgO/GE. The absorption spectrum covers the visible light range for both systems. We find that the GW gap of MgO@BLG (Fig. 8h) is around 2 eV greater than that of the MgO/GE system. These optical properties indicate the importance of vDW crystals, especially 2D MgO flakes, in nanooptoelectronic applications. Our DFT results for the optical properties of heterostructures of graphene and MgO suggest that integration of 2D materials enhances light–matter interactions, which offers a 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. Our results demonstrate that extremely large pressures are exerted on MgO nanoclusters between BLG – in close agreement with experiments – which can modulate the 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-layers of MgO flakes, 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 studies 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 of the symmetry of the π-states of graphene while the magnitude of p-doping in graphene per adsorbate unit remains nearly constant for the added network layers.

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 manifesting 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 offers more active sites and could dramatically alter their electronic and optical properties. Also, localized defects in hexagonal boron nitride and in functionalized BN cause a single-photon emission at room temperature, which has applications in bio-imaging and biosensing. 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.

Author contributions

F. S. and R. S designed the research; F. S., J. B., and 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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