Modulation of the band gap of graphene oxide: The role of AA-stacking

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ABSTRACT
The unique electronic properties of graphene make it an advantageous material for use in many applications, except those that require a band gap. Much work has been done to introduce an appropriately tuned band gap into graphene, including uniaxial strain and oxidation, with varying levels of success. We report here that the stacking configuration of the sheets in multilayered graphene oxide can have a significant impact on the band gap. Through comparison of X-ray absorption near-edge spectra of multilayered pristine graphene sheets with spectra simulated using density functional theory, we have found that AA-stacking pushes unoccupied states closer to the Fermi level than AB-stacking by widening the $p^*$ resonance in both graphene oxide and graphene. If the near-Fermi states have been removed such that the nearest unoccupied state to the Fermi level is the $p^*$ band, then AA-stacked multilayered graphene oxide will have a smaller band gap than AB-stacked graphene oxide. We have confirmed this by measuring the band gap of graphene oxide and reduced graphene oxide indirectly using X-ray absorption near-edge spectroscopy and X-ray emission spectroscopy. Controlling the stacking configuration of multilayered graphene oxide may provide a novel method for tuning its band gap.

1. Introduction
Graphene is a monolayer of graphite wherein the carbon atoms form a two-dimensional (2D) hexagonal structure (the honeycomb lattice). The material is of great interest because of its exceptional electrical, mechanical and thermal properties. Graphene has been suggested for use in technological applications such as nanoelectronics, sensors, supercapacitors, and hydrogen storage [1–3]. In applications to photovoltaics, graphene-based materials have been used as a light collector in organic solar cells [4], as a transparent conductor to replace the ubiquitous ITO [5], and as an intermediate conducting layer in tandem solar cells [6]. Many techniques have been developed to make graphene sheets, such as mechanical cleavage of graphite, chemical vapor deposition, and thermal fusion of polycyclic aromatic hydrocarbons. Among them, the most promising method for mass production of graphene is exfoliation of graphite oxide in a polar solvent, followed by reduction of the harvested graphene oxide (GO) sheets, although many methods have been proposed to accomplish this [7,8]. However, more than just a precursor material for graphene, GO itself has very interesting
properties and can be used in polymer composites [9] and dielectric layers in electronic devices [10]. Indeed, GO has shown to be a better transparent conducting film than graphene in solar cell applications [11,12]. GO can be applied used in various biological applications [13], for example, GO–Fe3O4 nanoparticles can be used for drug delivery and release [14].

For electronic device applications [15], a band gap is required to control the type and concentration of carriers, however, graphene is a zero-gap semiconductor [16]. There are numerous methods by which one may introduce a band gap into graphene [17,18]. However, a natural point where one may study how to engineer the band gap of graphene is GO, given its role in the preparation of graphene. GO has a finite electronic band gap due to oxidation of the carbon basal plane by oxygen-containing functional groups: phenol, hydroxyl, and epoxide groups on the plane and carboxylic groups at the lateral edge [19,20]. Interestingly, the effect that the stacking arrangement of the graphene oxide sheets has on the band gap of multilayered GO has not been studied, despite the fact that π–π overlap between graphene and functionalizing adsorbed aromatics is known to alter electrical characteristic of graphene [21]. There are many possible graphene stacking configurations, but two of the most important are the AB-stacking (Bernal stacking) and the AA-stacking configurations. The two stacking configurations are shown in Fig. 1. The images in Fig. 1 were made using VESTA [22]. AB-stacking is the lowest-energy configuration, and this is the dominant stacking mode found in highly-oriented pyrolytic graphite (HOPG). It is known that the way in which graphene sheets stack has a significant impact on the vibrionic structure of multilayered graphene sheets [23]. Given that the states that frame the band gap in GO will also be located in the interplanar region, it stands to reason that the way in which the layers interact will affect the band gap. This work studies that very interaction.

We have been studying the many facets of the electronic and physical structure of graphene oxide [24]. Here, we probe the band gap of multilayered GO (simply referred to as GO henceforth) and GO that has been reduced with hydrazine hydrate (rGO). The band gap is studied indirectly through a combination of X-ray absorption near-edge fine structure (XANES), to probe the unoccupied partial density of states (pDOS), and non-resonant X-ray emission spectroscopy (XES), to probe the occupied pDOS. Plotted on a common energy scale with respect to the core hole, the band gap is the energy separation between XES and XANES. These techniques boast site- and chemical-specificity that other techniques do not possess, and the transition probabilities are not modified by Franck-Condon factors like optical gap measurements, allowing for a detailed and unambiguous study of the carbon states that populate the near-Fermi energy regime.

2. Experimental

2.1. XES measurements

The XES measurements on the carbon 1s edges were performed at Beamline 8.0.1 at the Advanced Light Source at the Lawrence Berkeley National Laboratory using the soft X-ray fluorescence (SXF) endstation [25]. Emitted radiation was measured using a Rowland circle type spectrometer with a large spherical grating and a photon-counting area detector. The total experimental resolution was 0.3 eV FWHM. The fluorescence measurements were made using a depolarized configuration, which means that the vector E of the incidence beam lies at the scattering plane, i.e. \( p \)-polarization was used. The SXF endstation is configured such that the path of the emitted photons that can be detected by the spectrometer and the incident beam are perpendicular to each other.

2.2. XANES measurements

High-resolution XANES spectra on the C 1s edge were measured at the Spherical Grating Monochromator (SGM) beamline at the Canadian Light Source [26]. The GO X-ray absorption near-edge spectra (XANES) were measured in total electron yield (TEY) and total fluorescence yield (TFY) modes. The graphene XANES spectra, however, were also measured in partial fluorescence yield (PFY) mode. The PFY spectra were measured using a silicon drift detector (SDD) that acted as a very low-resolution spectrometer (FWHM \( \approx 150 \) eV). Integrating all counts detected by the SDD would yield a TFY spectrum, whereas isolating only the emission line from carbon produces a C 1s PFY spectrum. This was necessary in this case because the graphene and multilayered graphene samples were mounted on SiO2 substrates. Second order contamination from the monochromator allows for near-resonant excitation of the O sites in the SiO2 substrate, as the O 1s absorption threshold lies at nearly twice the energy of the C 1s edge. Although second order light from the monochromator is significantly weaker than the first order light that resonantly excites the graphene, the SiO2 substrate has orders of magnitude more oxygen than the graphene layers has carbon. Thus, O Kα emission from the substrate strongly competes with the C Kα emission from the graphene.

For normalization, in all cases, the PFY, TFY, and TEY spectra were normalized to the current generated in a photodiode when this photodiode was exposed to the incident beam. This photodiode current spectrum was not taken simultaneously with the sample spectrum, but rather directly afterwards. This technique allows one to directly measure the light intensity hitting the sample as a function of energy. This method allows one to correctly account for intensity fluctuations in the incident beam due to carbon contamination on all optically active beamline components. Such contamination can introduce false features into carbon spectra.

Fig. 1 – The AB- and AA-stacking configurations for graphite and multilayered graphene.
2.3. Graphene synthesis

Eight samples of pristine graphene mounted on SiO₂ substrates were prepared: two each of graphene, bilayered graphene, multilayered graphene with four to six layers, and multilayered graphene with ten or more layers. One sample from each of the four pairs was annealed at 900 °C. The graphene samples were grown using the atmospheric pressure chemical vapor deposition (APCVD) method. Copper foil (from Nilaco, 99.96%) with a thickness of 100 μm was used as the substrate for monolayer graphene growth; bilayer and multilayer graphene was grown on 70 μm copper foil. The chamber was preheated to 1060 °C with 1000 sccm of Ar and 200 sccm of H₂ and annealed for 40 min. After that, the rate of gas injection was altered depending on the desired characteristics of the graphene film. In the case of monolayer graphene, the H₂ gas injection rate was reduced to 10 sccm from 200 sccm, and 3 sccm of methane gas was injected. For bilayer graphene, the H₂ and methane gas injection rates were 70 sccm and 30 sccm, respectively. The growth time for both mono and bilayer graphene was 5 min. For multilayered graphene, we maintained 200 sccm of H₂ gas flow and injected only 3 sccm of methane. Growth time was increased to 15 min. Methane and H₂ gas inflows were then stopped and the sample was cooled down to room temperature. After growth, the finished samples were transferred to SiO₂ substrates using copper etchant.

3. Results

The GO sample was prepared as in the manner of GO paper from water filtration. The rGO sample was prepared as the first, but during the process, the water was substituted with DMF and hydrazine was added. The sample was heated and reduced in solution, then finally filtered. Further details on the general synthesis technique are published elsewhere [27,28]. These samples were chosen because reduction of GO is a necessary step if one wishes to achieve graphene from graphene oxide. Incomplete reduction can provide a way to modulate the oxidation level, and thus the band gap of GO.

As mentioned earlier, we probed the electronic states of the two samples using XES and XANES for the purposes of determining the band gap. The XES spectra were measured at Beamline 8.0.1 at the Advanced Light Source [25], while the XANES spectra were measured at the SGM beamline at the Canadian Light Source [26]. Fig. 2 shows the results of our experiments. In this Figure, the non-resonant C Kα XES spectrum and the C 1s XANES spectrum from each sample is plotted on the same energy axis, each in a separate panel. In terms of the energy axis, both the C 1s XANES and the C Kα XES spectra are both measured with respect to the C 1s core state. Thus, aligning the XANES and XES spectra on the same energy axis simply requires each to be calibrated to a known reference. All XANES spectra shown in this work were aligned to a sequentially measured XANES spectrum of HOPG. All XES spectra were similarly aligned to HOPG.

The XANES spectra were measured in both total electron yield (TEY) and total fluorescence yield (TFY) modes. The TEY technique involves counting electrons emitted from the sample via Auger decay, whereas the TFY technique requires one to count the photons emitted from the sample via radiative decay. Ideally, the intensity of emission of both electrons and photons scales linearly with the number of core holes created. When this holds true, TEY and TFY are both direct measures of the true absorption profile. In practice, however, there are two important caveats. The escape depth of Auger electrons is very shallow, which means that TEY spectra are very surface-sensitive. TFY is much more bulk-sensitive due to the longer escape depth of the emitted photons. However, when exciting the sample on a strong resonance, such as the C 1s-2p* feature in graphite, the rate of core hole creation does not increase linearly with a concomitant increase in absorption cross-section, and the TFY signal saturates at strong resonance features [29]. This leads to a characteristic
substrates were prepared: 

The second derivative method was chosen to analyze the band gap of GO. The second derivative is particularly useful for analyzing the pre-edge of a spectrum because weak but sharp features show much more prominently in the second derivative than broad yet strong features. This property helps to extract details from the near-Fermi portions of the XES and XANES spectra. Other researchers have successfully determined the band gaps of various materials indirectly using a combination of XANES and XES [32–34]. Calculating the second derivatives of XANES and XES spectra has proven to be an accurate and highly reproducible method of finding the band onsets, and thus the band gaps [35–38].

Minima in the second derivative correspond to features (maxima) in the spectrum. The band gap is therefore the energy separation between the highest-energy minimum in the second derivative of an XES spectrum (denoted $d^2XES/dE^2$) and the lowest-energy minimum in second derivative of an XANES spectrum. Depending on how the XANES spectrum is measured (TEY or TFY), the second derivative is denoted $d^2TEY/dE^2$ or $d^2TFY/dE^2$.

With this understanding of the second derivative method in mind, let us turn to the $d^2XES/dE^2$, $d^2TEY/dE^2$, and $d^2TFY/dE^2$ spectra of GO and rGO, displayed within the insets of each panel in Fig. 2. Before a discussion concerning the band gaps of the samples can begin, however, the differences in the $d^2TEY/dE^2$ and $d^2TFY/dE^2$ spectra of each sample is striking, particularly in the 284.5–286.5 eV range. For both samples, the $d^2TEY/dE^2$ shows only one minimum, at about 285.2 eV, whereas the $d^2TFY/dE^2$ shows a double-dip structure, with one minimum at 284.6 eV, the other at 285.6 eV. This double-dip structure in the TFY is not due to saturation, as saturation effects, the displayed TFY spectra have been treated using the correction method of Eisebitt et al. [30,31].

Neither is the difference in shape due to a normalization artifact from a contaminated mesh, as all XANES spectra were normalized using an asynchronously measured photodiode spectrum of the incident light to act as a background reference [39]. Thus the difference in shape between the TEY and TFY spectra is real and inherent. For rGO, there is a similar structure in the 284.5–286.5 eV range as indicated by dashed lines in Fig. 2, but the problem does not affect the determination of the band gap because both $d^2TFY/dE^2$ and $d^2TEY/dE^2$ have minima at 283.3 eV. This leads to a band gap of about 0.3 eV. However, the determination of the band gap for GO is not so simple, as it is not obvious, at this point, which minima of the three available one should use. The three possible band gaps, based upon the three candidate minima at 284.6 eV, 285.2 eV, and 285.6 eV, are labeled with arrows in panel (a) in Fig. 2.

Note that Fig. 2 shows many spectral differences between the spectra of GO and rGO, particularly in the range between 287 eV and 290 eV. This energy range is home to the spectral signatures of oxidizing functional groups [40–42,24]. The 287–290 eV energy range holds key information about the chemical character of the sample in question, but it is not relevant to a study of the band gap of graphene oxide. Therefore, we do not discuss it.

We thus present two fundamental questions: (1) Why do the TEY and TFY spectra have such different structure, as shown by their second derivatives? (2) Which local minimum does one use for the determination of the band gap of GO? Neither question can be answered until it is known what is causing the double-dip structure in the TFY of both samples. As we shall show later, the answers to both of these questions involves the AA-stacking mode, and in particular, how this configuration behaves when subjected to pressure within the bulk of a material.

3.1. Pristine graphene

The first step to answer the two questions stated above is to determine whether the double-dip structure is due to functionalization, or if one can see this structure in pristine multilayered graphene. To test this possibility, eight samples of pristine graphene mounted on SiO$_2$ substrates were prepared: two each of graphene, bilayered graphene, multilayered graphene with four to six layers, and multilayered graphene with ten or more layers, hereafter referred to as Gr, 2Gr, 4Gr, and 10Gr. The first set taken as is, and the second was annealed at 900°; further details of the synthesis can be found in mind, let us turn to the $d^2XES/dE^2$, $d^2TEY/dE^2$, and $d^2TFY/dE^2$ spectra of each sample in the bottom halves of the bottom two panels. (A colour version of this figure can be viewed online.)
in the Experimental section. Fig. 3 displays XANES spectra measured from the samples with different numbers of pristine graphene layers, as well as HOPG. The spectra of the multilayered graphene samples were recorded in both TEY and PFY modes; the fluorescence spectrum of HOPG was recorded in TFY mode. The reason for the difference in fluorescence measurement technique is explained in Section 2.

As one can clearly see, there are very few features in the 287–290 eV energy range in the graphene spectra, particularly for the annealed samples. This marks a sharp contrast with the GO samples, but the difference is expected. No spectral features within this energy range indicate that the samples have not been functionalized. However, there is another marked difference between the graphene and GO samples worthy of mention: the PFY and TEY spectra of the graphene samples are very similar in shape. This similarity is to be expected because of the thinness of the graphene samples. The saturation effects that strongly distort the TFY spectra of GO in Fig. 2 are only problematic for samples that are thicker than the penetration depth of the incident radiation, which is on the order of 100–200 nm for soft X-rays.

Saturation effects do not distort the PFY spectra of the graphene samples and thus the PFY and TEY spectra are much similar in shape. However, the PFY and TEY spectra are not identical, particularly when comparing the PFY and TEY spectra of the multilayered graphene samples. One can immediately see that features b at 284.8 eV and c at 285.4 eV that constitute the double-dip structure in the d2TFY/dE2 of GO shown earlier are seen again. The double dip is seen most strongly in the d2PFY/dE2 spectra of both 10Gr samples. It would seem that, as one adds layers, the double-dip structure becomes more prominent in the d2PFY/dE2 spectra measured from the sample. This trend is strongly supported by the HOPG results. However, another pattern also emerges. In the second derivative, the minimum at 284.8 eV becomes prominent while the largely positive feature at 286.3 eV (feature d) is suppressed; the two spectral changes happen simultaneously, suggesting a common cause. As layers are added, spectral weight is being added at both 284.8 eV and 286.3 eV.

It is therefore clear that, as one adds more graphene layers, more states are added at both 284.8 eV and 286.3 eV. Indeed, HOPG also shows prominent dips in its d2TFY/dE2 at these energies, a sample that is highly non-functionalized and has been subjected to none of the chemicals involved in either the creation of GO, or the transfer of graphene. An as-yet unidentified layer-dependant phenomenon is affecting these changes. Note that other researchers have noticed features in the 284.6–286.3 eV energy range. Indeed, the d2TEY/dE2 and d2PFY/dE2 spectra of the non-annealed monolayer graphene sample also show a feature a a dip 284.9 eV. In this case, the feature at 284.8 eV is likely caused by another effect, such as scattering from point defects, or doping from adsorbed gases or solvents. Whatever the source, it is mitigated by annealing, as this feature is sharply reduced in the spectra from the annealed monolayer graphene. Spectral weight in the 284.6–284.9 eV energy range is thus likely a composite from many contributions, but it is the layer-dependent one that we seek here.

4. Discussion and analysis

The double-dip structure has now been seen in GO, rGO, and multilayered pristine graphene if one stacks up 10 or more layers. Given that this structure occurs in pristine graphene and HOPG, it is not due to oxidation. This conclusion is supported by the fact that all prevalent functional groups identified on graphene oxide, namely carboxyl, hydroxyl, epoxide, and carbonyl, all have their characteristic resonances in the oxidation zone between 286 eV and 290 eV, and this energy region quite devoid of features. If the double-dip structure is not a chemical artifact, could it be due to structural differences, such as the interplanar stacking order?

We present a theoretical study of the effect of the stacking order on the electronic structure of multilayered graphene, in which we explicitly consider the AA- and AB-stacking configurations. Fig. 4 shows simulated XANES spectra of several structures, including graphene, AB- and AA-stacked bilayer graphene, and AB- and AA-stacked graphite; all simulations were performed using the WIEN2k code using the local density approximation (LDA) exchange–correlation functional. For all multilayered configurations, the interplanar spacing was optimized. The AB-stacked graphite had an optimized interplanar spacing that was very close to the experimental value of 3.348 Å, which is the reason why the LDA functional was chosen. The Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) exchange–correlation functional did not report an optimal interplanar spacing. The AB-stacked bilayer graphene also had a calculated optimal interplanar spacing very close to the known value for bulk graphite. This result agrees with previous studies [43]. However, the AA-stacked configurations all prefer to be much further apart. Separate calculations at 3.348 Å, the interplanar spacing preferred by AB-stacked graphite, and at the optimized spacing of ~3.6 Å were performed.

The simulations in Fig. 4 show three very important results. First, the π* band of graphene, as well as that of bilayer and infinite layer stacked graphene (graphite) in the AB-stacking configuration, has one major feature. In the second derivative, this feature produces one minimum in each case. Second, the π* band of bilayer and infinite layer graphene (graphite) shows a much broader lineshape; in the second derivative, this yields two local minima. Third, the relative spacing of the AA-stacked minima (and hence the width of the π* band) increases with an increasing number of layers and a decreasing interplanar spacing. If one were to increase the spacing to infinity, the double peak structure in the second derivatives of the bilayer graphene simulated XANES spectra would eventually coalesce into one feature, as one expects from graphene. In the AA-stacking bulk limit, when the interplanar distance equals that of AB-stacked graphite of 3.348 Å, the minima in the second derivative of the simulation line up quite well with the minima at 284.7 eV and 286.4 eV of the d2TFY/dE2 of highly-oriented pyrolytic graphite (HOPG), as shown in Fig. 4. Thus, it would seem that they layer-dependant effect that produces spectral weight at 284.7 eV and 286.4 eV is due to interactions between AA-stacked graphene sheets, whereas the minimum at 285.4 eV is due to AB-stacking.
The evidence is clear that double dip structure seen in the $d^{2}\text{TFY}/dE^2$ of multilayered graphene is due to spectral contributions from both AA- and AB-stacking. These simulations are compared to experimental spectra of graphene and HOPG. Vertical lines highlight important features in the experimental spectra; for consistency, the features are labeled identically to those in Fig. 3. (A colour version of this figure can be viewed online.)

Controlling the stacking configuration of a multilayered GO sample gives the device fabricator another means by which the band gap may be tuned, in addition to simply controlling the oxidation level [44,45]. In short, the stacking order adjusts the width of the $\pi^*$ band, which therefore controls the band gap if the sample is oxidized and the near-Fermi states have been removed.

AA-stacked GO therefore has a smaller band gap than AB-stacked GO. However, there is more to the story. The theoretical results displayed in Fig. 4 clearly show that the $\pi^*$ band widens as one brings sheets of graphene together in an AA-stacked order, which is markedly different behavior than that exhibited by the AB-stacked variety. The implications of this are immediate. If the $\pi^*$ band widens if AA-stacked sheets are brought closer to one another, then if one has a primarily AA-stacked sample of multilayered graphene oxide, then one may widen the $\pi^*$ band and thus narrow the band gap simply by applying external pressure along the c-axis. In short, AA-stacking may provide a way to externally control the band gap of GO.

Indeed, the sensitivity of the width of the $\pi^*$ feature in AA-stacked multilayered graphene to pressure along the c-axis explains why it is that the characteristic AA-stacked signal is not seen in TEY spectra. As mentioned earlier, multilayered graphene, if stacked in the AA configuration, is in its lowest energy state if the sheets are farther apart (about 3.58 Å) than if stacked in the AB configuration. The AA-stacked zones do not transition to AB-stacking; there is no phase change. Rather, the AA-stacked zones near the surface have the freedom to expand and have larger interplanar spacing. This larger spacing, in keeping with the results shown in Fig. 4, allows for a smaller $\pi^*$ bandwidth, and thus the near-surface AA-stacked regions show XANES spectra that look much like the AB-stacked zones. TEY is highly surface sensitive, and would see only the expanded AA-stacked zones. Deeper within the sample, however, the freedom to expand would not exist for any AA-stacked region. Such AA-stacked zones would be forced by the neighboring AB-stacked majority to assume a nominal layer separation of 3.348 Å, which leads to the detectable widening of the $\pi^*$ resonance feature in the bulk-sensitive TFY and PFY spectra of multilayered graphene, HOPG, and GO.

However, there is still an issue to address. The double-dip structure that is supposedly due to AA-stacking is an important component of the GO TFY spectra shown in Fig. 2 despite the fact that multilayered GO is known to have much greater interplanar spacing to accommodate the attached functional groups. The mechanism that allows for AA-stacking characteristics to appear in multilayered GO with large interplanar spacing is not understood at this time. However, it is clear that after reduction, minima at 284.6 eV and 286.5 eV become very prominent in the $d^{2}\text{TFY}/dE^2$ of rGO. Minima at these energies are due to AA-stacking, as we have already shown. It would appear that AA-stacking is perhaps the dominant stacking order in GO, much more so than in multilayered graphene. The reason for the preferred AA-stacking order, as well as the extent of the interplanar interaction in highly oxidized GO samples, are subjects that require further study.
5. Conclusions

We have found that the stacking configuration of the sheets in multilayered graphene and GO has a strong effect on the shape of the main $\pi^*$ feature. Fluorescence yield XANES measurements of graphene, multilayered graphene, and HOPG have shown that spectral weight at 286.3 eV and 284.7 eV arises as a function of number layers. Through density functional theory simulations, we have shown this spectral weight is due to AA-stacking. Although there are other effects that can introduce spectral weight at either 286.3 eV or 284.7 eV, AA-stacking can explain both simultaneously, which is important, given that they arise simultaneously. AA-stacking can introduce spectral weight at 286.3 eV or 284.7 eV, and the external pressure along the surface near-Fermi states have been lost due to oxidation, then one can tune the band gap by controlling the stacking. The stacking configuration allows for an additional degree of freedom when designing an appropriate band gap.

The sensitivity of the band structure of AA-stacked multilayered graphene, and by extension the band structure of AA-stacked multilayered GO, to interplanar spacing leads to an exciting possibility: a band gap that is easily modulated by the external pressure along the c-axis. There has been much research into opening a band gap in graphene or bilayer graphene using stress, but most efforts have been to stress the sheet in a direction within the basal plane [46–49]. There also has been some theoretical work into introducing a band gap in bilayer graphene using stress parallel to the surface normal, but the strains necessary were in the range of 30–50% [50]. However, we suggest going in the opposite direction: beginning with a wide bang gap, apply stress to close it. According to our results, a device constructed of few-layered GO, if constructed in an AA-stacking regime, would have a tuneable band gap. This gap may close as the layers are compressed in the c-axis direction, because adding external compression on the AA-stacked GO would push more states towards the Fermi level, as the simulations in Fig. 4 suggest. Comparing the two AA-stacked graphite calculations (one with an interplanar spacing of 3.348 Å, the other with 3.578 Å), a strain of 7% could potentially close the band gap by 0.2 eV.

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