Graphene/MoS$_2$ van der Waals Bilayer as the Anode Material for Next Generation Li-ion Battery: A First-Principles Investigation

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Abstract

We performed density functional theory (DFT) calculations for a bi-layered heterostructure combining a graphene layer with a MoS$_2$ layer with and without intercalated Li atoms. Our calculations demonstrate the importance of the van der Waals (vdW) interaction, which is crucial for forming stable bonding between the layers. Our DFT calculation correctly reproduces the linear dispersion, or Dirac cone, feature at the Fermi energy for the isolated graphene monolayer and the band gap for the MoS$_2$ monolayer. For the combined graphene/MoS$_2$ bi-layer, we observe interesting electronic structure and density of states (DOS) characteristics near the Fermi energy, showing both the gap like features of the MoS$_2$ layer and in-gap states with linear dispersion contributed mostly by the graphene layer.

Our calculated total density of states (DOS) in this vdW heterostructure reveals that the graphene layer significantly contributes to pinning the Fermi energy at the center of the band gap of MoS$_2$. We also find that intercalating Li ions in between the layers of the graphene/MoS$_2$ heterostructure enhances the binding energy through orbital hybridizations between cations (Li adatoms) and anions (graphene and MoS$_2$ monolayers). Moreover, we calculate the dielectric function of the Li intercalated graphene/MoS$_2$ heterostructure, the imaginary component of which can be directly compared with experimental measurements of optical conductivity in order to validate our theoretical prediction. We observe sharp features in the imaginary component of the dielectric function, which shows the presence of a Drude peak in the optical conductivity, and therefore metallicity in the lithiated graphene/MoS$_2$ heterostructure.

Introduction

Currently, Li-ion batteries (LIB) are a very popular power source for portable electronic devices and hybrid vehicles. However, despite being renewable and environmentally friendly, conventional Li-ion batteries are still far from meeting the national US ABC target for a cheap ($150/KWh) and high capacity (3000 KWh/Kg) power source. This is mostly due to the widespread use of
graphite based anodes in LIB, which only have a small theoretical specific capacity (372 mAh/g). Thus, the development of the next generation LIB calls for identifying alternative materials for the negative and positive electrodes. In this respect, both graphene and MoS$_2$ monolayers have demonstrated potential as materials for designing superior electrodes with high specific capacity. High capacities from 600 to 1000 mAh/g has been observed for single atomically thin graphene nanosheets. Moreover, several experimental works on transition metals and metal oxides supported on graphene as negative electrodes have shown enhanced performance for LIB. On the other hand, the usage of a transition metal sulfide MoS$_2$, with graphene like structure, was proposed as a potential anode material in a patent in 1980. Despite its high insertion capacity (≈1000 mAh/g), MoS$_2$ alone has not been realized as the primary anode material due to its low cyclic stability.

In this Letter, we construct van der Waals layers as the 'intercalating compound' using graphene and MoS$_2$ bilayer. Our density functional theory (DFT) calculations show orbital hybridization between the layers, where the vDW interaction dominantly contributes to the stability of the heterostructure with significant binding energy. A shift in chemical potential is also observed in our calculations for the graphene/MoS$_2$ bilayer when compared with the isolated graphene or MoS$_2$ mono layers. Particularly noticeable is the linear dispersion in the DOS near the Fermi energy of the graphene/MoS$_2$ bilayer, which resembles that of the isolated graphene monolayer. Thus, combining graphene with a MoS$_2$ layer helps to pin the chemical potential near the gap center of MoS$_2$ and creates semi-metal like electronic structure in the heterostructure.

Our DFT calculation shows an even larger binding energy when the graphene/MoS$_2$ bilayer are intercalated with Li ions. The higher stability in such heterostructure makes it a potential candidate for designing LIB anodes with larger specific capacity and longer cycle life-time. The hybridization between carbon $p$, lithium $s$, and molybdenum $d$ orbitals causes the chemical potential to shift into the $d$-bands making the Li intercalated heterostructure fully metallic. The resulting enhancement of the conductivity in lithiated graphene/MoS$_2$ heterostructure is highly desirable for the anode materials in LIB.

Earlier theoretical works have demonstrated similar chemical potential shift using various adatoms in addition to Li, for single and bilayer graphene. For a related graphene and MoS$_2$ heterostructure, Miwa et al. reported the DFT calculated density of states without observing any Fermi energy pinning or linear dispersion near the gap center of MoS$_2$. In this Letter, we have demonstrated, for the first time, the interesting Dirac dispersion characteristics in the electronic DOS of graphene/MoS$_2$ bilayer at the Fermi energy. Although the lithiation makes the compound metallic as expected, discharging of LIB gradually turns the anode into semimetal while retaining the stability. In the language of electrochemistry, such processes can be presented by the following two half-reactions:

\[
\begin{align*}
\text{In anode:} & \\
x\text{LiC}_6/\text{MoS}_2 & \xrightleftharpoons{\text{charge}} x\text{Li}^+ + xe^- + C_6/\text{MoS}_2, \\
\text{and in cathode:} & \\
x\text{Li}_1-x\text{CoO}_2 + x\text{Li}^+ + xe^- & \xrightleftharpoons{\text{discharge}} \text{LiCoO}_2
\end{align*}
\]

Therefore, our proof-of-principles calculations demonstrate the Li intercalated graphene/MoS$_2$ bilayer as potential candidates for designing high
performance anode materials for the next generation LIBs.

Computational Methods

All calculations in this paper are performed using the plane-wave pseudo-potential code VASP\textsuperscript{14-16} under the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE).\textsuperscript{17} For atomic core-levels, we have used projected augmented wave (PAW) potentials\textsuperscript{18,19} treating the 2s2p of C, 2s of Li, 4p5s4d of Mo, and 3s3p of S as the explicit valence electrons. For all calculations, the total energy during electronic relaxation is converged to 10\textsuperscript{-6} eV while the force/atom during ionic relaxation is converged to 0.01eV/Å. A maximum energy cutoff of 500 eV is used for plane-wave basis set.

In the xy-plane, 6x6 unit cells of graphene and 5x5 unit cells of MoS\textsubscript{2} are placed in a super-cell with \(a=b=16\ \text{Å}, \ c=40\ \text{Å}, \ \alpha = \beta=90^\circ, \text{ and } \gamma=120^\circ\). In our calculations, the Li atoms are intercalated between the graphene and MoS\textsubscript{2} layers at the center of the graphene honeycomb sites. For different metal ions, this location has been shown to have the largest binding energies by Chan et al.\textsuperscript{11} We have placed 12 Li atoms homogeneously in our super-cell. This sparse distribution of Li atoms approximates the interaction of isolated Li atoms with graphene and MoS\textsubscript{2}. The distance between Li atoms are large enough (\(\approx 7\ \text{Å}\)) to minimize the orbital overlap between neighboring Li atoms.

To incorporate the vdW interaction between the graphene and MoS\textsubscript{2} layers, we have used optB86b-vdW functional where the exchange functionals were optimized for the correlation part.\textsuperscript{20} Therefore, the LDA correlation part present in the PBE functional is removed by using the parameter AGGAC = 0.000 in the input file in order to avoid double-counting.

Calculations for the isolated 6x6 graphene, 5x5 MoS\textsubscript{2}, and 6x6 graphene + Li adatoms were performed using the same sized super-cell. For ionic relaxation of graphene + Li, graphene + MoS\textsubscript{2}, and graphene + Li + MoS\textsubscript{2} systems, we have used the \(\Gamma\) point to sample the Brillouin zone, while for all other calculations, e.g., DOS and dielectric functions, we used equally distributed 80 \(k\)-points in the irreducible Brillouin zone.

Results and Discussion

To estimate the adsorption energy, we define,

\[
\Delta E = E_A + E_B - E_{A+B},
\]

where \(E_{A+B}\) is the total energy of the A+B composite system, and \(E_A/E_B\) is the total energy of the isolated A/B constituent system.

In Table 1, we present our DFT calculated total energy for graphene, MoS\textsubscript{2}, the graphene/MoS\textsubscript{2} heterostructure, and the lithiated graphene/MoS\textsubscript{2} heterostructure. Using Eq. (1), we calculate the binding energy between graphene and MoS\textsubscript{2} bilayer with and without Li ions in between. We have 25 Mo atoms in our supercell, and scaled the total adsorption energy to obtain \(\Delta E\) per Mo ion. We find the \(\Delta E\) per Mo ion is enhanced by about three times when Li intercalation is considered. Without Li atoms, the graphene and MoS\textsubscript{2} layers form a physisorbed heterostructure with \(\approx 0.1873\ \text{eV}\) adsorption energy per Mo ion, where the most important contribution comes from the surface van der Waals interaction. The adsorption energy significantly increases in the presence of intercalated Li ions, and these higher adsorption energies (0.6 eV per Mo ion or 1.26 eV per Li ion) suggest a more stable structure. At the same time, the small change in atomic positions during the ionic relaxation clearly indicates the process is dominantly van der Waals driven physisorption. Thus, the Li ions are easily separable and lithiation process can be reversed. This is a highly desirable criterion for LIBs during ionization-deionization process which enhances the cycle lifetime of batteries.

The electronic structure of the isolated graphene and MoS\textsubscript{2} monolayers is changed near the Fermi energy when they are assembled to form a van der Waals heterostructure. In [2] we present the DOS for the graphene/MoS\textsubscript{2} bilayer systems with and without lithiation and compare with the DOS of the constituent monolayers. A graphene monolayer is a two dimensional Dirac material with linear dispersion near the Fermi energy.\textsuperscript{21,22} This property manifests by the cone like feature in the
Table 1: Binding Energy of graphene and MoS$_2$ interface with and without Li intercalation using DFT+vdW

|                  | Graphene | MoS$_2$ | Graphene + Li | Graphene / MoS$_2$ | Graphene / MoS$_2$ + Li |
|------------------|----------|---------|--------------|---------------------|------------------------|
| Total Energy (eV)| -553.25348 | -414.14277 | -571.97493 | -972.07776 | -1001.27726 |
| Binding Energy (eV)| 0.1873 (per Mo ion) | 0.6064 (per Mo ion) | 1.2633 (per Li ion) |                      |                        |

Figure 2: (color online) (a) Total DOS (black) for graphene; (b) Total DOS (blue) for MoS$_2$; (c) Total DOS (red) for graphene/MoS$_2$ heterostructure, orbital projected $d$-DOS of Mo (blue), and $p$-DOS (black) for C; and (d) Total DOS (red), $d$-DOS (blue) of Mo in MoS$_2$, $p$-DOS (black) of C in graphene, and $s$-DOS (green) of Li in the lithiated graphene/MoS$_2$ heterostructure; the Fermi energy is at 0 eV, shown by the vertical dashed line. Total DOS in the unit cell (for (c) and (d)) are scaled down by a factor of 50 for visual clarity. Inset in (c) and (d) shows DOS near the Fermi level.

DOS of graphene at the Fermi energy as shown in [2](a).

On the other hand, MoS$_2$ monolayer is a direct gap semiconductor with $\approx 1.8$ eV band gap. In our DFT calculations, this band gap is estimated to be 1.4 eV as shown in [2](b). Due to the unfilled $d$-orbitals in Mo atoms, the semi-local DFT functionals are inadequate, and one can incorporate many-body corrections such as GW or hybrid functionals HSE which accounts for the missing 0.4 eV band gap in the conventional DFT. In the present proof-of-principles calculations, our findings should remain unaffected from such band gap correction, while incorporating these corrections in large supercell with vdW interaction would greatly increase the computational cost. Therefore, we neglect such band-gap corrections in our calculations.

We plot the total DOS of graphene/MoS$_2$ in [2](c) with solid red curve. To provide visual clarity, total DOS is scaled down by a factor of 50 while comparing with the partial $d$-DOS (blue) of Mo in MoS$_2$ and $p$-DOS (black) of C in graphene. We find the presence of both the Dirac-cone-like feature from graphene and a gap-like feature from MoS$_2$ at the Fermi energy of the composite bilayer of graphene/MoS$_2$. An enlarged version of these symmetric features in the DOS at $E_F$ is presented in the inset of [2](c). This finding can be interpreted as the Fermi energy pinning at the gap cen-
Figure 3: (color online) Calculated real (blue) and imaginary (red) part of the dielectric function for (a) graphene, (b) MoS$_2$, (c) graphene/MoS$_2$ bilayer, and (d) Li intercalated graphene/MoS$_2$ heterostructure. Due to the proportionality between optical conductivity and imaginary dielectric function, such results can be directly compared with experimental measurements. See the main text for details.

Conclusions

In this Letter, adsorption of graphene on a MoS$_2$ monolayer is studied using DFT-based first-principles theory with and without intercalated Li atoms. Formation of a stable heterostructure between the layers is observed, where the major contribution to binding comes from the vdW interaction. Our calculations show that the addition of the graphene layer pins the Fermi energy near the gap center of MoS$_2$. Precise identification of the Fermi energy opens up the potential applications for LIB anode material through the manipulation of electronic structure of various constituent element combination with graphene/MoS$_2$ bilayer. Lithium insertion or intercalation between graphene/MoS$_2$ bilayer is found to have a bind-
ing energy within the physisorption range in our calculations, which demonstrates their prospect as superior anode materials. Therefore, our proof-of-principles calculations of adsorption energy, structural stability, electronic structure, and optical properties in graphene/MoS\(_2\) heterostructure provides a basis for future experimental and theoretical study towards designing the next generation anodes for Lithium ion batteries.

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