Adsorption and diffusion properties of calcium ions at the van der Waals interface of NbSe$_2$-graphene 2D heterostructure for multivalent battery applications: density functional theory calculations

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Abstract

Multivalent-ion batteries such as calcium-ion batteries show promise as a high-density alternative to lithium-ion batteries which currently dominate the portable electronics market. In this work, the adsorption and diffusion properties of calcium ion at the van der Waals (vdW) interface of the 2D heterostructure formed by vertically stacking NbSe$_2$ monolayer and graphene were investigated via density functional theory (DFT) calculations. Results showed that calcium can be effectively adsorbed on the vdW interface of the 2D heterostructure, with the binding energy of most stable site at $-2.77$ eV, much higher than most metal ions’ binding on pristine graphene. Thus, the NbSe$_2$-graphene 2D heterostructure reinforced the binding of calcium ions at the interface. It is revealed that due to the random stacking nature of NbSe$_2$ and graphene, a multi-path minimum energy pathways were identified at the van de Waals region, with relatively low diffusion barriers of around 0.20–0.50 eV. These indicate the capabilities of the 2D vdW heterostructure for fast multivalent ionic mobility and charge-discharge rate, while maintaining strong binding at the vdW interface. The results reveal NbSe$_2$-graphene 2D vdW heterostructure’s potential as a promising anode material for multivalent battery applications.

1. Introduction

Graphene, which consists of a 2D sheet of covalently bonded carbon atoms, has been studied extensively for its unique properties that are comparable and oftentimes much better that known semiconducting surfaces [1, 2] as well as its application as electrodes in electrical and optical devices [3, 4]. Its isolation from graphite [5] in 2004 paved the way for the discovery and study of many two-dimensional (2D) materials. Although it is widely used as a material base for energy storage devices like lithium-ion batteries (LIBs) because of its high specific surface area, high thermal stability, electroconductivity, and elastic moduli, studies have shown that Li capacity of pristine graphene, limited by lithium clusterization and phase separation, is lower than that offered by intercalation of lithium ion in graphite [6]. Furthermore, graphene is also found to have relatively low storage capacity and poor mechanical properties [7].

Researchers have been exploring various ways to overcome these shortcomings, one of which is the construction of heterostructures with other 2D materials such as oxides and dichalcogenides [8–11]. Transition metal dichalcogenides (TMDs) have been gaining attention recently for its potential applications in alkali metal ion batteries and multivalent batteries [12–14]. Building graphene and TMD heterojunctions not only addresses the aforementioned issues concerning graphene, but also concerns regarding TMDs’ inclination for aging with structural degeneration [15]. In addition, constructing heterostructures will not compromise the structural integrity of a material, and the original electronic properties can be maintained [15].
Rechargeable lithium-ion batteries (LIBs) remain to be the most prominent energy storage system in the portable electronics battery and electric vehicles market because of its high energy density, good rechargeability, and long cycle life. However, due to its relatively high cost, along with the ever-increasing demand for batteries with higher energy density, efforts have been made to identify alternatives and replacements to rechargeable LIBs [16–18]. At present, Li-air, Li-S, Na-ion, and multivalent ion batteries are considered to be promising alternative chemistries [18]. Multivalent ion batteries, specifically Mg$^{2+}$, Al$^{3+}$, and Ca$^{2+}$, have been garnering interests due to their natural abundance and stable multivalent states. Among the three mentioned, electrochemical systems employing calcium is capable of offering the highest voltage, with low redox potential comparable to that of lithium. However, developments in calcium-ion batteries have been slow, because of lack of suitable electrodes and the sluggish diffusion of calcium ions in most intercalation hosts [17].

In this study, the adsorption and diffusion of calcium ions in NbSe$_2$-graphene 2D heterostructure for multivalent battery applications is investigated to reveal their potential as electrode materials.

2. Methodology

The adsorption and diffusion of Ca ions on NbSe$_2$-graphene heterostructure was studied by performing first-principles calculations based on density functional theory using Quantum Espresso package [19]. Projector augmented wave (PAW) method [20], along with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [21], were utilized for the calculations. Convergence tests were performed to determine the optimum values for calculation parameters. Based on the convergence tests, the optimized energy cutoff for wavefunctions and charge density were found to be 60 Ry and 240 Ry, respectively. A 5x5x1 Monkhorst–Pack mesh was used in Brillouin zone sampling, and a vacuum spacing of at least 18.5 Å was considered to safely avoid interactions between the periodically repeating heterostructure. Grimme DFT-D3 corrections [22] were applied to take van der Waals interactions between graphene and NbSe$_2$ monolayers into consideration. Convergence threshold for self-consistency was set to 1.0D-6 Ry, and convergence threshold on total energy and on forces for ionic minimization were set to the default values of 1.0D-4 Ry and 1.0D-3 Ry/Bohr, respectively.

Due to differences in lattice parameters of NbSe$_2$ and graphene, a random stacking order of $2 \times 2 \times 1$ NbSe$_2$ and $3 \times 3 \times 1$ graphene was considered and optimized in all directions to obtain the most stable stacking configuration (figure 1). At the van der Waals interface, four stable adsorption sites were identified and considered (figure 1), namely; Site 1—in between the central portion of both the hexagonal structure of graphene and NbSe$_2$, Site 2—in between niobium atom and the lower portion of the graphene hexagon, Site 3—in between the carbon atom and the center of the NbSe$_2$ hexagon, and Site 4—in between niobium atom and the upper left portion of the graphene hexagon.

To calculate the average binding energy per monolayer of the vdW heterostructure, we used equation (1):

$$E_{bind} = \frac{E_{Total}(\text{NbSe}_2-\text{graphene}) - E_{Total}(\text{NbSe}_2) - E_{Total}(\text{graphene})}{2}$$  \hspace{1cm} (1)$$

where $E_{Total}(\text{NbSe}_2-\text{graphene})$ is the total energy of the NbSe$_2$-graphene heterostructure, $E_{Total}(\text{NbSe}_2)$ is the total energy of the NbSe$_2$ monolayer, and $E_{Total}(\text{graphene})$ is the total energy of pristine graphene. This average binding energy per monolayer can also be effectively interpreted as the average formation energy of the NbSe$_2$-graphene heterostructure.

Structural optimization was done on all sites, and the binding energy of calcium for each site is calculated using the formula:

$$E_{bind} = \frac{E_{Total}(\text{NbSe}_2-\text{graphene}) - E_{Total}(\text{NbSe}_2) - E_{Total}(\text{graphene})}{2}$$

Figure 1. (a) Top and (b), (c) side views of the optimized NbSe$_2$-graphene heterostructure, with an inter-monolayer distance of 5.21 Å, and lattice parameters 2.46 Å and 3.69 Å for graphene and NbSe$_2$, respectively. Graphene is represented by the brown atoms. Niobium-diselenide (NbSe$_2$) is represented by the green and light green atoms, respectively.
where $E_{\text{Total system}}$ is the total energy of the whole system and $E_{\text{Total (NbSe$_2$-graphene)}}$ is the total energy of the NbSe$_2$-graphene heterostructure without calcium. $E_{\text{cohesive (Ca)}}$ is the cohesive energy of calcium, and is calculated using the formula:

$$E_{\text{cohesive (Ca)}} = \frac{E_{\text{Total (Ca bulk)}} - 4E_{\text{Total (Ca atom)}}}{4}$$

where $E_{\text{Total (Ca bulk)}}$ is the total energy of calcium in bulk, and $E_{\text{Total (Ca atom)}}$ is the total energy of a single calcium atom.

The diffusion barrier values are calculated using cNEB method, with each path consisting of seven images. The charge distribution and transfer were studied quantitatively by Bader charge analysis [23]. All structures were visualized using VESTA [24].

### 3. Results and discussion

Among the two prominent allotropes (1T and 1H) of the NbSe$_2$ monolayer, 1H-NbSe$_2$ was chosen for our calculations because it is energetically more stable than the 1T structure and is metallic in nature [25, 26], which is appropriate for battery anode application. The optimized lattice constant of graphene and NbSe$_2$ monolayers are 2.46 Å and 3.69 Å, respectively. To construct the NbSe$_2$-graphene heterostructure, the graphene and NbSe$_2$ monolayers were vertically stacked (figure 1), and the NbSe$_2$ monolayer was biaxially strained by 7.27% in order to be accommodated to the supercell with graphene. In order to know which monolayer is to be strained, preliminary tests were performed, and results showed that in terms of total energy, strained graphene is higher in energy compared to strained NbSe$_2$ monolayer. The optimized heterostructure has an inter-monolayer distance of 5.21 Å and a calculated binding energy per monolayer of $-0.40$ eV which indicate a moderate interaction between the two monolayers.

For electrode materials, a relatively large binding energy is essential in the process of adsorption. One of the consequences of having a strong binding energy is that it allows the binding of higher calcium concentration at the van der Waals interface, which translates to high theoretical specific capacity. A high theoretical specific energy capacity combined with higher charge transferred per ion transport (compared to monovalent ions such as Li$^{+}$ and Na$^{+}$) implies a significantly higher capacity and more powerful battery system. Therefore, the adsorption properties of calcium on the interplanar space of the NbSe$_2$-graphene heterostructure was studied. Table 1 shows the binding energy of a single calcium atom with reference to bulk cohesive energy on Sites 1 to 4, as well as the bond length of Ca and the nearest Nb, Se, and C atoms in each of the sites. The binding energy of Ca

![Figure 2](image-url) Adsorption sites with optimized coordinates; namely (a) Site 1, (b) Site 2, (c) Site 3, and (d) Site 4. Graphene is represented by the brown atoms. Calcium is represented by blue atoms. Niobium diselenide (NbSe$_2$) is represented by the green and light green atoms, respectively.

| Ca position | Binding energy (eV) | Bond length (Å) | Ca-Nb | Ca-Se | Ca-C |
|-------------|---------------------|-----------------|-------|-------|------|
| Site 1      | $-2.77$             | 3.84            | 2.71  | 2.80  |
| Site 2      | $-2.55$             | 3.42            | 2.77  | 2.70  |
| Site 3      | $-2.68$             | 3.85            | 2.71  | 2.69  |
| Site 4      | $-2.55$             | 3.41            | 2.77  | 2.70  |
atom for Sites 1, 2, 3, and 4 are \(-2.77\) eV, \(-2.55\) eV, \(-2.68\) eV, and \(-2.55\) eV, respectively. In addition, the measured NbSe\(_2\)-graphene separation distance for Sites 1, 2, 3 and 4 are 5.70 Å, 5.95 Å, 5.84 Å, and 5.90 Å respectively. It is noted that the separation distance is correlated to the strength of the binding of the calcium ion at the van der Waals interface, such that a higher adsorption energy implies shorter separation distance between NbSe\(_2\) and graphene. The most energetically preferred site is Site 1. It can be inferred that the Ca atom prefers to adsorb on top of the hollow part of the NbSe\(_2\) hexagonal structure. Nevertheless, the adsorption energy values are close to each other, and can be effectively assessed as almost equivalent magnitude wise in terms of binding preference. Compared to bilayer graphene configuration, the NbSe\(_2\)-graphene heterostructure effectively strengthened the binding of metal ion such as calcium at the van der Waals interface. In a related work utilizing bilayer graphene, sodium adsorption energy at the van der Waals interface is very low at less than \(-1\) eV [27]. It was concluded that pristine bilayer graphene structure is not a good intercalation material for metal ions and further structural modification is necessary, such as the creation of defects. Such large binding energies are indicative that higher calcium coverages at the van der Waals interface is feasible and that theoretically, higher specific energy capacity can be achieved. Note that at high calcium coverages, calcium-calcium repulsion are more pronounced and thus, the binding energy tends to decrease. As such, although high calcium adsorption energy is correlated to high specific energy capacity, there is a limit as to the maximum calcium ions that an electrode material could hold as a result of repulsive interactions among the ions, and this would depend on the degree of adsorption of a single (or very low coverage) calcium ion.

Figure 3 shows the PDOS for Nb 4\(d\), Se 4\(p\), C 2\(p\) and Ca 4\(s\) states at the van der Waals interface of the NbSe\(_2\)-graphene-calcium system. It is observed that there is a significant states hybridization in the vicinity of the Fermi energy and even within the occupied states region. This gave rise to strong interactions at the van der Waals region and subsequently, high adsorption energy of calcium within the NbSe\(_2\)-graphene heterostructure. The mobility of Ca atoms on the NbSe\(_2\)-graphene heterostructure is another important factor for it being an ideal anode material of metal-ion batteries, which is closely related to its charge and discharge performance. A low diffusion energy barrier creates more mobility for calcium atoms. The diffusion energy barrier values of calcium, shown in figure 4, were calculated on three different paths using cNEB method; Path I: the Ca atom moving from Site 1 to Site 2, Path II: the Ca atom moving from Site 2 to Site 3, Path III: the Ca atom moving from Site 3 to Site 4. The calculated diffusion energy barriers for Paths I, II and III are as follows; 0.53 eV, 0.23 eV, and 0.36 eV, respectively. Based on the calculated ionic diffusion barriers, all paths are good conduction pathways for calcium diffusion. Path II is calculated to have the lowest diffusion barrier, thus is the most likely path where calcium ions will move during the charging-discharging process. The ionic diffusion energy barrier value calculated for Path II is comparable to Li diffusion barrier values in silicene [28], graphene [29], NbSe\(_2\) monolayer [30], and WS\(_2\)-NbSe\(_2\) 2D heterostructure [14], with values 0.23 eV, 0.28 eV, 0.21 eV, and 0.18 eV respectively. However, compared to other materials with relatively low barrier on most paths, calcium diffusion on NbSe\(_2\)-graphene heterostructure is less efficient in that there are less paths that have low diffusion barrier. Due to the random stacking pattern at the van der Waals interface, the effective diffusion barrier for calcium would be around 0.5 eV as given by Path I. Nevertheless, in terms of magnitude, the calculated values on Path II and even Path III are still reasonable to be compared with Li diffusion on other systems, and with temperature
effects, even the diffusion barrier on Path I can be overcomed. Table 2 shows the calculated charge transfer of calcium to its surrounding atoms via the Bader charge analysis. This data is supplemented by the charge difference isosurface plots in figure 5 with isosurface level of $0.002 \text{e}^{-}/\text{a. u.}$.3 The yellow regions denote electron rich-regions while the cyan regions imply electron depleted region. The charge density difference plot acquired indicates the electron transfer from calcium to its neighboring atoms, particularly selenium and carbon atoms. Furthermore, it can be inferred that the ionic interaction between calcium and the neighboring atoms resulted to some form of ionic bonds, binding Ca to C, Nb, and Se atoms at the van der Waals interface. Observation of the charge difference isosurface also indicate that the electron rich region (yellow regions) is more pronounced between Ca and NbSe$_2$ suggesting that Ca ion binds more strongly on the NbSe$_2$ side. This supports earlier

| Ca position | Charge Transfer (e) |
|-------------|---------------------|
| Site 1      | 1.40                |
| Site 2      | 1.42                |
| Site 3      | 1.41                |
| Site 4      | 1.42                |

Figure 4. Diffusion energy barrier of calcium and the transition states on three different paths; path I: Ca atom moving from site 1 to site 2, path II: Ca atom moving from site 2 to site 3, path III: Ca atom moving from site 3 to site 4.

Figure 5. Charge difference isosurface plot (side and top view) of calcium on NbSe$_2$-graphene 2D-heterostructure on (a, b) site 1, (c, d) site 2, (e, f) site 3, and (g, h) site 4. Cyan represents regions of electron depletion while yellow represents regions of charge gain upon Ca adsorption on the heterostructure. Isosurface level: $0.002 \text{e}^{-}/\text{a. u.}$.3 The structures were visualized using VESTA.
studies wherein graphene was found to be less adsorbent to metal ions. As such, building a 2D heterostructure with graphene solves the issue of small binding energy but retains the high ionic conductivity that graphene provides.

4. Summary and conclusion

In summary, calcium adsorption and diffusion at the van der Waals interface of NbSe$_2$-graphene 2D heterostructure were explored and analyzed. Our calculations revealed that the most stable configuration of NbSe$_2$-graphene 2D heterostructure is the one in which the $2 \times 2 \times 1$ NbSe$_2$ monolayer is strained to fit the $3 \times 3 \times 1$ graphene supercell. Moreover, the calculated formation energy per monolayer of the 2D heterostructure is moderate at $-0.40$ eV. Moreover, DFT calculations showed that calcium can be effectively adsorbed at the vdW interface of NbSe$_2$-graphene heterostructure, with Site 1 in between the hollow part of both hexagonal structures as the most energetically preferable site for adsorption. The calculated lowest diffusion barrier of 0.23 eV for Path II is comparable to that of graphene, silicene, NbSe$_2$ monolayer, and WS$_2$-NbSe$_2$ heterostructure, while the effective diffusion energy barrier is modest at 0.50 eV. The charge difference isosurface plots show the transfer of electrons from calcium to its neighboring atoms, indicating the formation of ionic interactions that binds the Ca atom to C, Nb, and Se atoms at the vdW interface of the heterostructure. The isosurfaces also show that stronger interaction between calcium ion and NbSe$_2$ is present, thereby reinforcing the adsorption as compared to just pristine graphene monolayer.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of interest

The authors declare that they have no conflict of interest.

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