GeSe/BP van der Waals Heterostructures as Promising Anode Materials for Potassium-Ion Batteries

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ABSTRACT: Potassium-ion batteries have attracted attention because of their abundant resources and similar electrochemistry to Li-ion batteries (LIBs). In the present work, GeSe/black phosphorus (BP) heterostructures as promising anode materials for K-ion batteries (KIBs) have been systematically investigated by first-principles calculations. The results reveal that GeSe/BP exhibits a semiconductor-to-metal transition after incorporating K atoms, indicating enhanced conductivity compared to monolayer GeSe. The energy barrier for K atom diffusion on GeSe/BP surface is relatively lower than that on monolayer GeSe. In addition, the GeSe/BP heterostructure can accommodate up to five layers of K atoms with negative adsorption energy, which greatly improves the storage capacity. Hence, the GeSe/BP heterostructure has great potential for application in advanced electrode materials in KIBs.

INTRODUCTION

Since the 21st century, Li-ion batteries (LIBs) have widely been used in the field of mobile phones, laptops, cameras, and rechargeable vehicles owing to their high energy density, high reversible capacity, long cycle life, large electromotive force, and light weight. However, because of some intrinsic limitations such as high cost and scarcity of Li in the earth’s crust, the current LIBs are less feasible for large-scale stationary energy storage systems (ESSs). In order to further facilitate the application of ESSs, K-ion batteries (KIBs) have attracted attention because of their abundant resources and similar electrochemical performance to LIBs. Moreover, a K atom has a lower redox potential than a Na atom (−2.92 V vs −2.71 V), which leads to higher energy density and a wide voltage window. Thus, KIBs have a better prospect for application in ESSs. However, only a limited number of studies for KIBs have been reported compared to LIBs, mainly because of the limited choice of anode materials. For example, graphite cannot be used as an anode of KIBs because embedding K atoms are thermodynamically unfavorable. Hence, it is still challenging to obtain new efficient electrode materials for KIB systems with high electronic conductivity and excellent cycling stability and rate capability.

Recently, monolayer GeSe, a monolayer group-IV monochalcogenide with phosphorene-like structure, has attracted wide attention because of high electronic performance and less toxicity. Made from an earth-abundant element, the GeSe nanosheet with a thickness less than 1 nm has been successfully synthesized and explored for fabricating various nanodevices in the laboratory. Besides, monolayer GeSe exhibits a robust direct band gap and strong anisotropic transport property with a high hole mobility of 4.71 × 10^3 cm^2/V s, which makes it a promising candidate for future application in integrated circuits and optoelectronic devices. Moreover, because of the unique structural and excellent transport properties, monolayer GeSe is considered as an ideal anode material in rechargeable LIBs. However, monolayer GeSe has a lower storage capacity of 176.78 mA h g\(^{-1}\) and poorer conductivity compared to metal anode materials for KIBs. Therefore, we explored a new system using a two-dimensional (2D) material as the substrate and build a heterostructure, which could improve the storage capacity.

Black phosphorus (BP) has entered the scope of our consideration because of its graphite-like multilayered structure and excellent electronic properties such as high carrier mobility and high on/off ratio as field-effect transistors. Because of the puckered honeycomb structure of monolayer BP, a fast Li\(^+\) diffusion and large Li capacity can be achieved for lithium intercalation. The high theoretical capacity of 2596 mA h g\(^{-1}\) could be attained in the uptake of lithium to form Li\(_3\)P. In addition, monolayer BP demonstrates great mechanical and dynamical stabilities. However, BP can be easily oxidized after exposed to air within several hours and thus cannot be used directly as an anode material. Monolayer BP could be a good substrate for GeSe as KIBs because of similar structural and electronic properties. Hence, the following study aimed at improving the performance of GeSe as an anode material.

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In this study, we have systematically investigated the adsorption and diffusion properties of K atoms on the GeSe/BP heterostructure by using first-principles calculation. The results show that after K adsorption, the conductivity of GeSe/BP heterostructure can be greatly enhanced, the energy barrier of K diffusion on GeSe/BP surface is reduced, and the storage capacity of K is increased. This work provides key insights into GeSe/BP van der Waals (vdW) heterostructure and examines its potential applications as an anode material for KIBs with high electrical conductivity and capacity.

## COMPUTATIONAL METHODS

In the study, the first-principle calculations were performed by the Vienna Ab initio Simulation Package (VASP) with the projector augmented wave method based on density functional theory (DFT). The Perdew–Burke–Ernzerhof (PBE) scheme within the generalized gradient approximation (GGA) was used to treat the exchange–correlation interaction of electrons. The empirical correction scheme proposed by Grimme was chosen because of the nontrivial vdW interaction. The cutoff energy for the wave function was set to 500 eV and the force criterion for the structural relaxation was chosen as 0.01 eV Å⁻¹. A Monkhorst–Pack k-point mesh of $3 \times 3 \times 1$ was respectively used to calculate the properties of all studies in the 2D Brillouin zone. To avoid the interaction between neighboring layers, a vacuum spacing of 30 Å was added along the direction perpendicular to the 2D nanosheet. The charge density difference was calculated by CASTEP code in this work.

For adsorption and diffusion properties of K atoms, a $3 \times 2 \times 1$ supercell of GeSe/BP heterostructure was chosen to guarantee enough area for K atoms to move. To find out the minimum energy path (MEP) and saddle points between the initial and final positions and calculate the migration energy barrier for K diffusion, the climbing image nudged elastic band (CI-NEB) method was employed. CI-NEB, which is a small modification of the NEB method, is efficient in determining the transition states and MEPs for both fixed cell and generalized solid-state transformations. Subsequently, three or four intermediate images were linearly interpolated between two stable states.

## RESULTS AND DISCUSSION

The GeSe/BP heterostructure is achieved by monolayer GeSe and BP stacked in the vertical direction with the consideration of vdW interactions between layers. The calculated lattice parameters of monolayer GeSe ($a = 3.96$ Å, $b = 4.16$ Å) and BP ($a = 3.34$ Å, $b = 4.62$ Å) are in good agreement with the experimental and other theoretical calculations. In this study, three stacking patterns are considered according to the relative position of GeSe and BP, which are shown in Figure 1. The Ge or Se atom above the center of BP hexagon (hole) is labeled H; the monolayer GeSe directly and completely located above the monolayer BP is labeled T; the Ge or Se atom above the mid-point of the P–P bond of BP is labeled B. After structural optimization, GGA-PBE calculations show that the total energy of H-style is 0.028 and 0.029 eV lower than that of T-style and B-style, and thus, H-style is the most stable stacking pattern. Hence, the H-style is chosen as the stacking model in the following calculations. The mismatch in the a and b directions is a bit larger than 5%, but it will not influence the stability of the heterostructure because of the flexible puckered structure of monolayer GeSe and BP.

To further check the stability of the heterostructure and determine the interlayer interaction intensity quantitatively, the binding energy ($E_b$) per unit cell is calculated by the following formula:

$$E_b = E_{\text{GeSe}/\text{BP}} - E_{\text{GeSe}} - E_{\text{BP}}$$

where $E_{\text{GeSe}/\text{BP}}$, $E_{\text{GeSe}}$, and $E_{\text{BP}}$ represent the total energy of the GeSe/BP heterostructure, isolated monolayer GeSe, and BP, respectively. The calculated value of binding energy ($E_b = -0.346$ eV) is negative, which indicates that the GeSe/BP heterostructure is energetically stable.

Next, we have investigated the K adsorption/diffusion behaviors on the H-style GeSe/BP heterostructure to evaluate the usage as a flexible anode material for KIBs. For BP as the substrate of the GeSe nanosheet, two typical adsorption sites are considered in this study: (1) K adsorbed on the surface of GeSe (labeled K/GeSe/BP) and (2) K embedded in the interlayer of GeSe/BP (labeled GeSe/K/BP). According to the minimum energy principle, the most stable adsorption sites of K atoms on both K/GeSe/BP and GeSe/K/BP systems are very similar to pristine monolayer (K/GeSe and K/BP). For K/GeSe/BP, there is one possible adsorption site for K atoms on the surface and with K adsorbed above the center of...
triangle Ge–Se rings (H$_0$-site); for GeSe/BP, there are two possible adsorption sites for K atoms between the layers of GeSe/K/BP: one is above the center of triangle Ge–Se rings (H$_1$-site) and the other is the adsorption above the center of the triangle P–P rings (H$_2$-site), as shown in Figure 2. Besides, some other adsorption sites have also been considered in order to verify the above results, as can be seen in Figure S1. All adsorption sites of K atoms on the heterostructure are fully optimized, and no obvious structural changes are observed. In order to find out the most stable adsorption site of K adsorption, we have calculated the adsorption energy ($E_{\text{ads}}$) of these three sites by the following formula:

$$E_{\text{ads}} = (E_{\text{GeSe/BP}+K} - E_{\text{GeSe/BP}} - nE_K)/n$$

(2)

where $E_{\text{GeSe/BP}+K}$, $E_{\text{GeSe/BP}}$, and $E_K$ are the total energy of K atoms on the GeSe/BP heterostructure, GeSe/BP heterostructure, and a single K atom in the same size of the supercell, respectively, and $n$ is the number of K atoms. On the basis of the definition, a larger negative value of $E_{\text{ads}}$ suggests a stronger affinity of K atoms bonded with the heterostructure and thus a more stable system, which indicates that the GeSe/BP heterostructure is feasible as KIB anodes. From the comparative $E_{\text{ads}}$ diagram of all adsorption sites in Figure S1 and Table 1, the H$_0$ site and H$_1$ site are the most stable adsorption sites for K/GeSe/BP and GeSe/K/BP systems, respectively. Figure 3 shows the differential charge density of K atoms located at the H$_0$ site and H$_1$ site of the GeSe/BP heterostructure systems (K/GeSe/BP and GeSe/K/BP). For both cases, the loss of electron is denoted by red and the gain of electron is denoted by blue. As can be seen from Figure 3a, the net loss of electronic charge is found directly above the K atoms and the gain of electronic charge is found on their adjacent layers. Because the electronegativity of Ge (Se) is larger than K, the electrons transfer from K atoms to adjacent Ge and Se atoms forming strong ionic bonds. However, there is no electron accumulation in the BP layer because of the comparatively long distance between K and BP layer. Figure 3b shows that the electrons transfer from K atoms to both GeSe layer and BP layer, as the electronegativity of P is larger than K, which indicates the strong ionic bonding between the embedded K atom and the two layers.

To determine the ion bond strength quantitatively, we calculate the value of $\Delta Q$ between the K atom and GeSe/BP by the Mulliken charge analysis, and the results are summarized in Table 1. As one K atom is adsorbed on the outside surface of GeSe, the calculated charge on K is $+0.75\,\text{e}$, whereas the corresponding charge of GeSe and BP is $+0.23\,\text{e}$ and $-0.98\,\text{e}$, respectively. Hence, the charges of K atoms and GeSe are transferred to the below BP layer. Besides, as one K atom is embedded in the interlayer of GeSe/BP, the charge transfer of K to GeSe and BP is $-0.2\,\text{e}$ and $-1.04\,\text{e}$, respectively. The BP layer gained obviously more charge.
compared to GeSe, which is mainly because of the stronger electronegativity of the P atom. It can be seen clearly that all the configurations show the charge transfer from K to GeSe/BP heterostructure, strongly indicating the ionic interactions between K and GeSe/BP heterostructure.

To investigate the conductive properties and the electronic structure of GeSe/BP upon K atom intercalation, the magnitude of quantum conductivity ($G$) function, electron density of states (DOS), and partial DOS (PDOS) of GeSe/BP, K/GeSe/BP, and GeSe/K/BP systems are calculated, as shown in Figure 4. The magnitude of $G$ function is calculated to evaluate the conductive property after adsorption by the Landauer formula:

$$G = G_0 \sum_{i=1}^{N} T_i$$  \hspace{1cm} (4)

where $T_i$ is the transmission probability of the $i$th channel, $N$ is the number of propagating modes crossing Fermi energy ($E_F$), and $G$ is a constant ($G_0 = 2e^2/\hbar$, where $e$ denotes the electronic amount and $\hbar$ is the Planck constant). In the case of a perfect ballistic transport, no scattering is considered, namely, $T_i$ is always unity. According to the Landauer formula, the number of bands crossing the Fermi level $E_F$ (Figure S2) contributes to the number of conductional channels or the size of $G$. The calculated $G$ values of K/GeSe/BP and GeSe/K/BP with all conductional channels are shown in Figure 4a,b. The $G$ values crossing the Fermi level $E_F$ of GeSe/BP, K/GeSe/BP, and GeSe/K/BP systems are $0 \times G_0$, $4 \times G_0$, and $5 \times G_0$ respectively. Therefore, K/GeSe/BP and GeSe/K/BP have higher conductivity than GeSe/BP.

In Figure 4c, the largest peak of DOS below $E_F$ is located between 0 and $-1.885$ eV for GeSe/BP, between $-0.222$ and $-2.522$ eV for K/GeSe/BP, and between $-0.457$ and $-2.786$ eV for GeSe/K/BP. The largest peak is slightly red-shifted and the conduction band proportions of the system increase after K adsorption, which implies that the charge transfer and the stability of the system slightly enhances. For GeSe/BP (Figure 4d), the state near the Fermi level is nearly flat and with a narrow and indirect band gap of 0.347 eV, which is slightly smaller than that of monolayer GeSe (1.100 eV) and BP (1.042 eV) (Figure S3). It is worth noting that the relative small band gap of GeSe/BP is greatly beneficial for electrode conductivity. For K/GeSe/BP and GeSe/K/BP systems, both of them have no band gap and become metallic after potassiation process. Thus, the problem of poor electronic conductivity can be solved by using BP nanosheets as a substrate of monolayer GeSe, completing the requirement of high electronic conductivity for anode materials. This phenomenon is also found in a MoS$_2$/graphene heterostructure, which is converted from semiconducting to metallic after lithiation. In addition, it can be seen from Figure 4e that the orbitals of K overlap with both Ge and Se as K atoms are...
adsorbed on the GeSe surface (K/GeSe/BP), which is the feature of covalent hybridization interactions. As K atoms are embedded into the interlayer of GeSe/BP (GeSe/K/BP), the orbitals of K overlap with both GeSe and BP, indicating the covalent hybridization of embedded K with GeSe and BP as can be seen in Figure 4f. Although the bond between K and GeSe/BP is dominated by ionic interactions, some covalent components still cannot be ignored.

As the rapid charge and discharge capabilities of KIBs are closely related to the diffusion properties, we further analyze the diffusion energy barrier for one K atom at the GeSe/BP heterostructure. The adsorption of the K atom on the GeSe surface and interlayer of GeSe/BP is discussed individually. The most stable K adsorption site, the possible diffusion paths, and the energy barrier of K on the GeSe surface are first studied, which are similar to that of monolayer GeSe. The path between two adjacent H1 sites along the groove of the GeSe surface is chosen for K diffusion, as shown in Figure 5. As the K atom diffuses on the outside surface of GeSe, it can be seen that the K atom overcomes two Ge−Se bands (band S1 and band S2), producing two similar high peaks (0.095 eV), which is slightly smaller than monolayer GeSe (0.132 eV). It can be considered that the K atom interacts only with the GeSe layer because the BP layer is far from the K atom. The barrier of K diffusion is relatively lower on the GeSe surface, mainly because the interaction of BP substrate with GeSe by vdW force weakens the stronger K bonds with the GeSe surface.

Then, we have investigated the diffusion path and the energy barrier of K atoms in the interlayer of GeSe/BP. Two adjacent H1 sites are chosen as reference because of a larger negative $E_{\text{ads}}$ than the H2 site, and the diffusion path is along the direction (H1−S1−S2−H1). There is only one peak with an energy barrier of 0.226 eV because of the collective interaction of K with both layers, as can be seen in Figure 6. Consequently, the formation of the GeSe/BP heterostructure increases the energy diffusion barrier of monolayer GeSe from 0.132 to 0.226 eV. However, it is still lower than some other Li diffusion barriers in monolayer GeS (0.236 eV), graphene (0.277 eV), and GeSe (0.329 eV).49−54 The diffusion barrier suggests that the depotassiation processes on the GeSe/BP heterostructure are energetically favorable, indicating that GeSe/BP is a reliable anode material.

After investigating the adsorption site and diffusion path, the storage capacities of K with higher concentration are considered next. To explore the maximum storage capacity for K atoms, we have calculated the average adsorption energy of K atoms as a function of its concentration (x) on three sides of GeSe/BP heterostructure: GeSe surface, BP surface, and interlayer, as can be seen in Figure 7. The $E_{\text{ads}}$ values of interlayer (6 K atoms), two surfaces (12 K atoms), and three sides (18 K atoms, as can be seen in Figure 7a) by filling all the stable adsorption sites with K atoms are −1.724, −1.449, and −1.29 eV, respectively. These negative adsorption energies can ensure good adsorption stabilities of potassiation on GeSe/BP. It can be found that $E_{\text{ads}}$ decreases with the increasing of K contents because of the enhancement of K−K repulsion at a relatively higher K concentration. In order to further improve the level of storage capacity for K, another K adsorption layer (30 K atoms) above the remaining center of triangle Ge−Se or P−P rings has covered on the outside surface of GeSe and BP separately, as can be seen in Figure 7b. The distances between the outermost K layer and the second outer K layers are 3.817 and 3.924 Å, whereas the distances between the inner K layer and the host GeSe or BP are 2.625 and 2.508 Å, respectively. Though the outermost two K atom layers are slightly far away from GeSe/BP, the calculated $E_{\text{ads}}$ is still negative with a value
show that GeSe/BP has great potential for application in high-capacity (capacity than monolayer GeSe. Meanwhile, the maximum layer. It can be inferred that the GeSe/BP heterostructure can energetically stable. The outermost layer of K possesses a lower 20, K atoms on GeSe/BP is evaluated to be 313.67 mA h g\(^{-1}\). The authors acknowledge the support by National Natural Science Foundation of Shaanxi province, China Science Foundation of China (NSFC, no. 51471124), Natural Science Foundation of Shaanxi province, China (2017QJ045), the Fundamental Research Funds for the Central Universities (no. xj2016018), and the National Undergraduate Training Program for Innovation and Entrepreneurship (201810710128).

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