Investigation of Boron-Doped Graphdiyne as a Promising Anode Material for Sodium-Ion Batteries: A Computational Study

Sobira Gharehzadeh Shirazi, Mokhtar Nasrollahpour, and Mohsen Vafaeef

ABSTRACT: In this work, by density functional theory (DFT) calculations, sp−sp2-hybridized boron-doped graphdiyne (BGDY) nanosheets have been investigated as an anode material for sodium storage. The density of states (DOS) and band structure plots show that substituting a boron atom with a carbon atom in an 18-atom unit cell converts the semiconductor pristine graphdiyne (GDY) to metallic BGDY. Also, our calculations indicate that, due to the presence of boron atoms, the adsorption energy of BGDY is more than that of GDY. The diffusion energy barrier calculations show that the boron atom in BGDY creates a more suitable path with a low energy barrier for sodium movement. This parameter is important in the rate of charge/discharge process. On the other hand, the projected density of states (PDOS) plots show that sodium is ionized when adsorbed on the electrode surface and so Na−BGDY interaction has an electrostatic character. This type of interaction is necessary for the reversibility of adsorption in the discharge mechanism. Finally, the calculation of the theoretical capacity shows an increase in BGDY (872.68 mAh g\(^{-1}\)) in comparison with that in GDY (744 mAh g\(^{-1}\)). Thus, from comparison of different evaluated parameters, it can be concluded that BGDY is a suitable anode material for sodium-ion batteries.

INTRODUCTION

Currently, fossil fuels provide a considerable part of the world’s energy supply.\(^1\) There are concerns about the increase in the concentration of greenhouse gases released into the atmosphere and the global climate changes resulting from the use of these fuels.\(^7\) Electrical energy storage (EES) can generate clean energy from the large-scale integration of variable renewable electricity sources (VRESs), such as wind, water, solar, and nuclear energies.\(^3\) Accordingly, these technologies decrease fossil fuel consumption and consequently reduce the generation of greenhouse gases.\(^1\) One of the first types of batteries used for EES is lithium-ion batteries (LIBs). They have been used widely as rechargeable storage devices in most of the electronic devices such as mobile phones, personal computers, and electronic vehicles because of their high capacity, long lifetime, and rate capability.\(^4\)\(^−\)\(^8\)

However, some concerns such as high price and limited lithium resources have been raised about continuing the production of LIBs.\(^7\)\(^−\)\(^10\)

Sodium-ion batteries (SIBs) have recently received tremendous attention as a promising alternative to LIBs because of the low cost of sodium (\(~\$150/ton\)) in comparison with lithium (\(~\$5000/ton\)) and more abundance of sodium resource.\(^4\)\(^−\)\(^9\)\(^\)\(^11\) A prevalent anode material of LIBs is graphite, which is less successful in accommodating Na ions and cannot be an appropriate candidate for SIBs.\(^12\)\(^−\)\(^13\) A Na ion has a larger radius (1.06 Å) than a Li ion (0.76 Å).\(^14\)\(^−\)\(^15\)

The small interlayer space of graphite (3.34 Å) can create a thermodynamic and kinetic limitation of sodium diffusion and adsorption in this structure.\(^16\)\(^−\)\(^19\) Thus, remarkable attempts have been made to find an appropriate negative electrode for SIBs.

Just like in LIBs, recent research studies have shown that two-dimensional (2D) materials, because of their outstanding structural and electronic features, have gained increasing attention as suitable candidates for SIBs.\(^20\)\(^−\)\(^23\) Most of the 2D materials can provide lower energy barriers for sodium-ion diffusion and larger surface areas for sodium storage in comparison with bulk materials.\(^23\)\(^−\)\(^25\) One such material is hybrid phosphorene/graphene nanocomposite, which was studied by Wang et al. using first-principles calculations.\(^5\)

They showed that the mechanical properties of phosphorene can be improved by introducing graphene layers between phosphorene layers. Therefore, sodium atoms can be incorporated between the phosphorene and the graphene layers with favorable adsorption energy. This investigation also showed that the computed specific capacity for this material was about 372 mAh g\(^{-1}\), which was more than that of the pristine phosphorene (324 mAh g\(^{-1}\)).\(^25\) Another type of 2D material is silicone/graphene heterostructure, which was
studied by Shi et al. They considered the feasibility of using a Si/G heterostructure as an anode electrode material for SIBs and LIBs by first-principles calculations. They calculated the theoretical capacity of 487 mAh g⁻¹ for lithium and sodium storage. Moreover, their results showed that this material can provide low energy barriers with appropriate diffusion paths for Li and Na ions. Some of the other 2D materials that have been investigated by DFT as SIB anodes are layered MoS2 (146 mAh g⁻¹), monolayer phosphorene (865 mAh g⁻¹), silicene (954 mAh g⁻¹), boron-doped graphene (762 mAh g⁻¹), β12 borophene and χ1 borophene (1240 and 1984 mAh g⁻¹, respectively), boron-doped graphyne (751 mAh g⁻¹), and among others.

GDY is one of the carbon allotropes that has been investigated as an anode material for LIBs. Also, this structure can be synthesized in different morphologies (such as nanotubes, nanowires, and nanowalls) by morphology-controlled syntheses, which are used as energy storage materials, highly efficient catalysts, and so on. It has been shown that GDY nanofilms with a conductivity of 2.516 × 10⁻⁴ S m⁻¹ have semiconductor properties. An investigation of GDY as an anode material for LIBs indicates an excellent capacity of 1388 mAh g⁻¹ for Li storage. The sp–sp²-hybridized GDY substructure was first synthesized by Haley et al. This structure is composed of a framework of sp and sp² carbon atoms that form two types of pores, as shown in Figure 1. One of them is a hexagonal ring (H site), and the other is a bigger trigonal pore (T site). A previous study of pristine GDY as an anode material for SIBs demonstrated that this structure had a theoretical capacity of 744 mAh g⁻¹ (LiC₄). BGDY is one of the graphdiyne derivatives. This structure has two known configurations. Wang et al. constructed one such structure, which was composed of equal large hexagonal pores. They investigated the storage of sodium in this structure and concluded that this newly synthesized material with high conductivity and a capacity of 1617 mAh g⁻¹ can be a suitable anode material for application in SIBs. Also, theoretical investigations on this type of BGDY have indicated a low diffusion energy barrier for ion mobility and a high theoretical capacity of sodium storage (818 and 1617 mAh g⁻¹ for different studies). Thus, this newly synthesized BGDY can be a promising anode material for SIBs. The structure of the other type of BGDY investigated in this work is composed of hexagonal rings and trigonal pores, which can be formed by the replacement of boron atom with carbon atom per 18-atom GDY unit cell. Figure 2 shows a 4 × 4 BGDY supercell with two different sites (T site and H site). As shown in the figure, each of them can be considered as a unit cell for the BGDY supercell.

In this study, using the first-principles calculations, we investigated the BGDY monolayer application as an anode material in SIBs. For this purpose, we estimate some important parameters such as adsorption energy of sodium atoms and the diffusion of sodium ions on a BGDY monolayer, electronic conductivity using band structure and DOS diagrams, and theoretical capacity. Furthermore, the interaction of sodium with both GDY and BGDY nanosheets is studied by PDOS plots to suggest the adsorption mechanism.

RESULTS AND DISCUSSION

Electronic Properties. Electronic conductivity is a significant factor to consider a structure as an electrode material for application in SIBs. In this research study, the band structure and DOS plots have been used to study the electronic properties of GDY and BGDY structures. By analyzing the DOS plot of the pristine graphdiyne (as shown in Figure 3a), we can conclude that the pristine graphdiyne with a closed-shell structure is a semiconductor having a band gap of about 0.5 eV, where the Fermi level is located in the middle of the band gap. This observation is consistent with the previous study. Replacing a boron atom instead of a carbon atom in each 18-atom unit cell of the GDY structure creates an electronic hole in the closed-shell electronic structure of GDY and shifts the Fermi level to the valance band. Therefore, as shown in Figure 3, we observed a transfer from a semiconductor GDY (Figure 3a) to a metallic BGDY (Figure 3b). On the other hand, the electron transfer on the electrode surface is the basis of the charge/discharge mechanism. Thus, by boron doping, we observed an improvement in the electron transfer phenomenon on the electrode surface.

Sodium Adsorption on the Surface of Monolayer BGDY/GDY. As shown in Figure 2, the BGDY supercells have two different sites, namely, T site and H site. These two sites are considered as active sites for the adsorption of sodium atoms. On the other hand, the T sites have two different positions for adsorption: in the corners and in the center of

---

Figure 1. Framework of GDY with sp and sp² carbon atoms.

Figure 2. Supercell of BGDY and two different types of unit cells.
this trigonal pore. Figure 4 shows three types of BGDY adsorption positions, A (top of H site), B (corners of T site), and C (center of T site). We investigated the energy and mechanism of sodium adsorption in these three sites by all atomic relaxations (Figure S1). Note that in the T site adsorption, the first sodium atom is placed at the center of the hole without height after relaxation (Figure S1b). An increase in the sodium concentration at this site leads to the adsorption of more sodium atoms away from the center. When the number of sodium atoms at the T site is six, the up and down of corners are fully occupied (Figure S1c−e).

Calculations indicate that the seventh and eighth sodium atoms are adsorbed on the first sodium layers exactly on the top of the T site center (Figure S1f). Table 2 shows the adsorption energies of these sites. These results show that the adsorption of one sodium atom on the T site is stronger than that on the H site. Two factors are responsible for this phenomenon: (1) T site has a larger diameter than H site and (2) T site has a lower electron charge density and so the number of electrons transferred at this site is more than that at the H site because the adsorption is due to the charge transfer from a sodium electron donor to a BGDY electron acceptor. Also, to show the effect of boron doping on adsorption energy, we investigated the adsorption of sodium on the T site and the H site of GDY and BGDY (see Table 3). The results show that owing to the presence of boron atoms with less electron charge density, BGDY has more electron affinity and subsequently higher adsorption energy than GDY. Boron atoms create an electronic hole in the closed-shell electronic structure of pristine GDY and subsequently increase the electron transfer from a sodium electron donor to the electronegative BGDY surface in the adsorption process. The PDOS plots (Figure 5) indicate the level of sodium ionization at each adsorption site of DGY/BGDY. As shown in these plots, in the H site and the T site of BGDY, the s-orbital peak of sodium is shifted toward the conductive band more than that of the corresponding sites in GDY. Thus, the degree of sodium ionization in BGDY is more than that in GDY. Also, in both structures, the degree of sodium ionization at the T site is higher than that at the H site. The peak of the s-orbital of isolated sodium in Figure 5a is referenced as the amount of peak shift and sodium ionization. Thus, in terms of adsorption energy, BGDY is better than GDY as an anode material for SIBs. On the other hand, at the T site, the average adsorption energy is decreased with an increase in sodium concentration. As the number of adsorbed sodium increases, the electron density on the surface is increased and the electronegativity of the surface and

Figure 3. Band structure and DOS plots of (a) GDY and (b) BGDY. The zero energy is set to the Fermi energy.

Figure 4. Three active adsorption sites (A, B, C) of the BGDY surface.

Table 1. Optimized Cell Parameters of GDY and BGDY

| structure | calculated cell parameter (Å) | previous studies (Å) |
|-----------|-----------------------------|----------------------|
| GDY       | 9.45                        | 9.48                 |
| BGDY      | 9.63                        | 9.38                 |

Table 2. Adsorption Energies of H Site and Different Concentrations of T Site

| number of sodium | T site adsorption energy (eV) | H site adsorption energy (eV) |
|------------------|-------------------------------|-------------------------------|
| 1 Na             | −4.12                         | −3.20                         |
| 2 Na             | −2.11                         | −2.38                         |
| 3 Na             | −2.21                         | not adsorbed                  |
| 4 Na             | −2.18                         | not adsorbed                  |
| 6 Na             | −1.91                         | not adsorbed                  |
| 8 Na             | −1.79                         | not adsorbed                  |

Table 3. Adsorption Energy and Adsorption Height for GDY and BGDY Unit Cells

|              | T site | H site |              | T site | H site |
|--------------|--------|--------|--------------|--------|--------|
|              | $E_{\text{ad}}$ (eV) | adsorption height (Å) | $E_{\text{ad}}$ (eV) | adsorption height (Å) |
| GDY          | −3.27  | 0      | −2.27        | 2.24   |
| BGDY         | −4.12  | 0      | −3.20        | 2.22   |
subsequently the adsorption energy are decreased (see Table 2).

For further investigation of the Na–BGDY interaction, we calculate the electron charge density of the sodiated structure. As shown in Figure S2, there is no covalent overlap between the charge density of sodium and BGDY atoms. Thus, adsorption of sodium on BGDY/GDY is physical and not chemical. Reversibility is one of the characteristics of physical

Figure 5. PDOS plots of (a) s-orbital of an isolated sodium atom, (b) Na@BGDY H site, (c) Na@BGDY T site, (d) Na@GDY H site and, (e) Na@GDY T site. The zero energy is set to the Fermi energy.

Figure 6. Out-of-plane diffusion through H site (TS denotes transition state).
adsorption. However, chemical adsorption is irreversible due to the high binding energy. Thus, adsorption of sodium on GDY/BGDY is physical and reversible.

**Diffusion Energy Barrier of Sodium Ions on the Monolayer BGDY.** Investigation of the mobility of sodium ions on the anode structure is a substantial issue and plays a significant role in the performance of SIBs. The calculation of diffusion energy barriers to finding a low energy pathway for the movement of sodium ions on the structure can help us better understand the charge/discharge rate.

Now, we investigate the migration behavior of sodium ions via two main kinds of diffusion paths: out-of-plane and in-plane diffusion. Climbing image nudged elastic band (CI-NEB) calculation was used to evaluate the diffusion energy barrier of sodium ions. In out-of-plane diffusion, a sodium ion migrates from one side to another side of the BGDY monolayer in the H site. Figure 6 shows this path and its energy barrier, which is about 29.43 eV. This energy is very large, and probably sodium ion cannot pass through this site without damaging the structure. On the other hand, there is no energy barrier to pass through the T site. Because the stable adsorption height of sodium at this site is zero, the sodium ion uses the T site to migrate from one side to another side of the structure.

In the in-plane diffusion, we consider two possible paths: (I) between two adjacent H site and T site (Figure 7) and (II) between two adjacent T sites (Figure 8). In the first case, the sodium ion starts to move from the top of the H site center toward the most stable position (T site) of the $4 \times 4$ supercell. In this path, a sodium ion passes through the top of the sp$^2$–sp$^2$ bond that creates an energy barrier of about 0.11 eV. In the second case, the initial and final stable positions are two adjacent T sites. There are three paths for sodium ion migration in this type of diffusion. Figure 8 demonstrates these paths and their energy barriers. In the first path (blue arrow), the sodium ion moves from the T site center, passes from the top of the boron atom, and reaches the final position in the center of the adjacent T site. In the second one (gray arrow), the sodium ion passes from above the C–C bond center that is located between two adjacent T sites. In the third path (orange arrow), the sodium ion goes through the top of the carbon atom. The energy barriers for these paths are about 0.55, 0.62, and 0.48 eV, respectively.

In the first case (H site to T site (Figure 7)), the low energy barrier is due to the instability of the H site adsorption compared with the T site adsorption. Also, the results of T site to T site diffusion indicate that passing the top of the boron atom has a lower energy barrier in comparison with passing the top of the carbon atom. This is due to the low electron density of the boron atom than that of the carbon atom, which tends to interact most with the sodium electron donor. Note that the low energy barrier of the C–C bond path is due to the higher electronegativity of the two sp$^2$-hybridized carbon atoms in comparison with boron atoms.

**Electron Charge Density.** To clearly show the effect of electron density on the adsorption energy and diffusion energy barrier, we performed an electron charge density calculation. Figure 9 shows the calculated electron charge density of the BGDY surface in the XY-plane. A comparison of adsorption energies, barrier energies, and electron charge density shows that the presence of boron atoms in BGDY creates an electron-less system and increases the adsorption energy in comparison with that of GDY. This figure shows that the T site has a very low electron charge density than the H site,
which is in agreement with the amount of adsorption energies. Also, BGDY, through the presence of boron atoms, creates a path with a low energy barrier and decreases the diffusion energy barrier.

Theoretical Capacity. To calculate the theoretical capacity, the maximum number of sodium atoms adsorbed on the BGDY surface is obtained. As shown in Figure 4, a $2 \times 2$ supercell of BGDY consists of four H sites and two T sites. In the section of the adsorption energy calculation (Table 2), we indicate that each H site and T site can adsorb at the most two and eight sodium atoms, respectively. Thus, a $2 \times 2$ supercell can store a minimum of 24 sodium atoms. Then, we add four sodium atoms to the structure. The calculations represent that 28 sodium atoms can be adsorbed on the BGDY surface without the clustering of sodium atoms (the energy of sodium clustering is $-1.13$ eV). Figure S3 shows the fully adsorbed BGDY structure and Table 4 shows the calculated adsorption energies of some of the low and high sodium concentrations. From this storage capacity, we obtained the theoretical capacity of 872.68 mAh g$^{-1}$, which is calculated by

$$C_t = \frac{nF}{M}$$

where $C_t$, $n$, $F$, and $M$ are the theoretical capacity, the number of electrons transferred in the electrochemical process, the Faraday constant, and the molecular mass of BGDY, respectively. The theoretical capacity of BGDY indicates an improvement in comparison with that of nondoped graphene. The more negative value of cohesive energy indicates higher stability of the structure. The results show that the stability of Na@BGDY decreases gradually with the increasing number of adsorbed sodium atoms. This is a promising result of using BGDY as an anode material in SIBs.

## COMPUTATIONAL METHOD

All our calculations have been performed within the density functional theory (DFT) framework and based on the plane wave basis set—self consistent field theory (pseudopotential) using the Quantum ESPRESSO package. DFT calculations in this study have been carried out by the projected-augmented wave (PAW) pseudopotential. Generalized gradient approximation (GGA) developed by Perdew–Burke–Ernzerhof (PBE) is used to calculate the electronic exchange–correlation energy. The semiempirical correction scheme of Grimme (DFT-D2) is adopted to define the van der Waals interaction between sodium and BGDY surface in both adsorption and diffusion mechanisms. Kinetic energy cutoff is optimized in 90 Rydberg to limit the Kohn–Sham wave functions. The numerical integration in the Brillouin zone (BZ) is performed using the Monkhorst–Pack grid of $10 \times 10 \times 1$. The optimized cell parameters of the hexagonal lattices of GDY and BGDY are 9.45 and 9.63 Å, respectively, which shows an expansion in the cell after boron doping. These optimized cell parameters are in agreement with previous works. Table 1 lists the relaxed cell parameters of GDY and BGDY. To avoid interactions of layers in the periodic boundary condition, the $c$ vector is considered to be 20 Å. The average adsorption energy of sodium on GDY and BGDY surfaces is defined as follows

$$E_{ad} = \frac{E_{\text{complex}} - (E_{\text{bare}} + nE_{Na})}{n}$$

where $E_{ad}$, $E_{\text{bare}}$, $E_{Na}$, and $n$ are the adsorption energy, the energy of the bare structure, the energy of the isolated single Na atom, the energy of adsorbed structures, and the total number of adsorbed Na atoms, respectively. $E_{\text{Na}}$ is calculated by putting up a single sodium atom at the center of a simple cubic lattice with the cell parameter of 19 Å. This large cell parameter is applied to avoid the interaction of sodium atoms in a periodic boundary condition.

The cohesive energies are obtained to study the stability of multiple sodium adsorbed structures as follows

$$E_{\text{coh}} = \frac{E_{\text{complex}} - (mE_C + nE_B + lE_{Na})}{(m + n + l)}$$

where $E_{\text{coh}}$, $E_{\text{complex}}$, $E_C$, $E_B$, and $E_{Na}$ are the cohesive energy and the energies of the Na–GDY/BGDY structures, the isolated carbon atom, the isolated boron atom, and the isolated sodium atom, respectively. Also, $m$, $n$, and $l$ are the number of carbon atoms, boron atoms, and sodium atoms, respectively. The more negative value of cohesive energy indicates higher stability of the structure.

The climbing image nudged elastic band (CI-NEB) method was utilized to find the pathway with the minimum energy barrier for Na ion diffusion. This method is based on acquiring the minimum energy barrier for sodium ion migration on BGDY between the initial and the final position.

## CONCLUSIONS

In summary, using density functional theory calculations, we concluded that doping of the closed-shell GDY by boron atoms leads to the improvement in the sodium storage.
capacity of this structure. By comparing the adsorption energy values, we showed that the sodium adsorption ability of BGDY is more than that of GDY. Also, the results of the diffusion energy barrier calculations indicate that boron atoms lead to a decrease in the activation energy for sodium ion migration between the active adsorption sites. The analyses of PDOS plots show that the adsorption phenomenon on BGDY and GDY is electrostatic and not covalent. This electrostatic interaction is critical for the reversibility of the charge/discharge process. On the other hand, from the PDOS plots, the amount of sodium ionization at the BGDY sites is more than that at the GDY sites, which is in agreement with the adsorption energy values. Finally, there is an increase in the theoretical capacity of BGDY (872.68 mAh g\(^{-1}\)) in comparison with that of GDY (744 mAh g\(^{-1}\)).

Thus, by a comparison with some other commercial ready electrode materials such as hard carbon,\(^{29,60}\) BGDY could show good performance in SIBs.

---

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00422.

Adsorbed sodium on the H site and different concentrations of adsorbed sodium on the T site; electron charge density of the H site and the T site adsorption; and fully adsorbed BGDY (PDF)

Author Information

Corresponding Author
Mohsen Vafaee — Department of Chemistry, Tarbiat Modares University, 14115-175 Tehran, I. R. Iran; orcid.org/0000-0002-4784-9074; Email: m.vafaee@modares.ac.ir

Authors
Sobira Gharehzadeh Shirazi — Department of Chemistry, Tarbiat Modares University, 14115-175 Tehran, I. R. Iran
Mokhtar Nasrollahpour — Department of Chemistry, Tarbiat Modares University, 14115-175 Tehran, I. R. Iran; orcid.org/0000-0002-2288-2070

Complete contact information is available at https://pubs.acs.org/doi/10.1021/acsomega.0c00422

Notes
The authors declare no competing financial interest.

Acknowledgments
We would like to acknowledge the High-Performance Computing (HPC) facilities of the Tarbiat Modares University. We also thank Mohammad Reza Hosseini for his guidance and helpful comments on this project.

References

(1) Yang, Z.; Zhang, J.; Kintner-Meyer, M. C.; Lu, X.; Choi, D.; Lemmon, J. P.; Liu, J. Electrochemical energy storage for green grid. Chem. Rev. 2011, 111, 3577–3613.
(2) Lu, J.; Li, L.; Park, J.-B.; Sun, Y.-K.; Wu, F.; Amine, K. Aprotic and aqueous Li–O2 batteries. Chem. Rev. 2014, 114, 5611–5640.
(3) Beaudin, M.; Zareipour, H.; Schellenberglabe, A.; Rosehart, W. Energy storage for mitigating the variability of renewable electricity sources: An updated review. Energy Sustainable Dev. 2010, 14, 302–314.
(4) Xu, J.; Wang, M.; Wickramaratne, N. P.; Jaroniec, M.; Dou, S.; Dai, L. High-performance sodium ion batteries based on a 3D anode from nitrogen-doped graphene foams. Adv. Mater. 2015, 27, 2042–2048.
(5) Wang, L.; Jiang, Z.; Li, W.; Gu, X.; Huang, L. Hybrid phosphorene/graphene nanocomposite as an anode material for Na-ion batteries: a first-principles study. J. Phys. D: Appl. Phys. 2017, 50, No. 165501.
(6) Etacheri, V.; Marom, R.; Elazar, R.; Salita, G.; Aurbach, D. Challenges in the development of advanced Li-ion batteries: a review. Energy Environ. Sci. 2011, 4, 3243–3262.
(7) Shi, L.; Zhao, T. Recent advances in inorganic 2D materials and their applications in lithium and sodium batteries. J. Mater. Chem. A 2017, 5, 3735–3758.
(8) Javidian, S.; Atashzar, S. M.; Gharibi, H.; Vafaee, M. Phosphorene and graphene flakes under the effect of external electric field as an anode material for high-performance lithium-ion batteries: A first-principles study. Comput. Mater. Sci. 2019, 165, 144–153.
(9) Kulish, V. V.; Maliy, O. I.; Persson, C.; Wu, P. Phosphorene as an anode material for Na-ion batteries: a first-principles study. Phys. Chem. Chem. Phys. 2015, 17, 13921–13928.
(10) Banerjee, S.; Neilsial, S.; Pati, S. K. First-principles design of a borocarbonitride-based anode for superior performance in sodium-ion batteries and capacitors. J. Mater. Chem. A 2016, 4, 5517–5527.
(11) Wang, N.; Li, X.; Tu, Z.; Zhao, F.; He, J.; Guan, Z.; Huang, C.; Yi, Y.; Li, Y. Synthesis and Electronic Structure of Boron–Graphdiyne with an sp-Hybridized Carbon Skeleton and Its Application in Sodium Storage. Angew. Chem., Int. Ed. 2018, 57, 3968–3973.
(12) Stevens, D. A.; Dahn, J. R. The mechanisms of lithium and sodium insertion in carbon materials. J. Electrochem. Soc. 2001, 148, A803–A811.
(13) Hong, S. Y.; Kim, Y.; Park, Y.; Choi, A.; Choi, N.-S.; Lee, K. T. Charge carriers in rechargeable batteries: Na ions vs. Li ions. Energy Environ. Sci. 2013, 6, 2067–2081.
(14) Xie, X.; Ao, Z.; Su, D.; Zhang, J.; Wang, G. MoS2/Graphene Composite Anodes with Enhanced Performance for Sodium-Ion Batteries: The Role of the Two-Dimensional Heterointerface. Adv. Funct. Mater. 2015, 25, 1393–1403.
(15) Slater, M. D.; Kim, D.; Lee, E.; Johnson, C. S. Sodium-ion batteries. Adv. Funct. Mater. 2013, 23, 947–958.
(16) Jache, B.; Adelhelm, P. Use of graphite as a highly reversible electrode with superior cycle life for sodium-ion batteries by making use of intercalation phenomena. Angew. Chem., Int. Ed. 2014, 53, 10169–10173.
(17) Senguttuvan, P.; Rousse, G.; Seznec, V.; Tarascon, J.-M.; Palacin, M. R. Na2Ti3O7: lowest voltage ever reported oxide insertion electrode for sodium ion batteries. Chem. Mater. 2011, 23, 4109–4111.
(18) Xiong, H.; Slater, M. D.; Balasubramanian, M.; Johnson, C. S.; Rajh, T. Amorphous TiO2 nanotube anode for rechargeable sodium ion batteries. J. Phys. Chem. Lett. 2011, 2, 2560–2565.
(19) Liu, H.; Jia, M.; Cao, B.; Chen, R.; Lv, X.; Tang, R.; Wu, F.; Xu, B. J. Nitrogen-doped carbon/graphene hybrid anode material for sodium-ion batteries with excellent rate capability. J. Power Sources 2016, 319, 195–201.
(20) Mortazavi, B.; Dianat, A.; Cuniberti, G.; Rabczuk, T. Application of silicene, germanene and stanene for Na or Li ion storage: A theoretical investigation. Electrochim. Acta 2016, 213, 865–870.
(21) Ling, C.; Mizzon, F. Boron-doped graphene as a promising anode for Na-ion batteries. Phys. Chem. Chem. Phys. 2014, 16, 10419–10424.
(22) Jing, Y.; Ortiz-Quiles, E. O.; Cabrera, C. R.; Chen, Z.; Zhou, Z. Layer-by-layer hybrids of MoS2 and reduced graphene oxide for lithium ion batteries. Electroc. Acta 2014, 147, 392–400.
(23) Tang, Q.; Zhou, Z. Graphene-analogous low-dimensional materials. Prog. Mater. Sci. 2013, 58, 1244–1315.
(24) Zhu, J.; Yang, D.; Yin, Z.; Yan, Q.; Zhang, H. Graphene and graphene-based materials for energy storage applications. Small 2014, 10, 3480−3498.

(25) Liu, X.; Wen, Y.; Chen, Z.; Shan, B.; Chen, R. A first-principles study of sodium adsorption and diffusion on phosphorene. Phys. Chem. Chem. Phys. 2015, 17, 16398−16404.

(26) Shi, L.; Zhao, T. S.; Xu, A.; Xu, J. B. Ab initio prediction of a silicene and graphene heterostructure as an anode material for Li-and Na-ion batteries. J. Mater. Chem. A 2016, 4, 16377−16382.

(27) Mortazavi, M.; Wang, C.; Deng, J.; Shenoy, V. B.; Medhekar, N. V. Ab initio characterization of layered MoS2 as anode for sodium-ion batteries. J. Power Sources 2014, 268, 279−286.

(28) Yang, E.; Ji, H.; Jung, Y. Two-dimensional transition metal dichalcogenide monolayers as promising sodium ion battery anodes. J. Phys. Chem. C 2015, 119, 26374−26380.

(29) Xu, S.; Fan, X.; Liu, J.; Jiang, Q.; Zheng, W.; Singh, D. J. Adsorption of Na on silicene for potential anode for Na-ion batteries. Electrochim. Acta 2019, 297, 497−503.

(30) Zhang, X.; Hu, J.; Cheng, Y.; Yang, H. Y.; Yao, Y.; Yang, S. A. Borophene as an extremely high capacity electrode material for Li-ion and Na-ion batteries. Nanoscale 2016, 8, 15340−15347.

(31) Nasrollahpour, M.; Vafaei, M.; Hosseini, M. R.; Iravani, H. Ab initio study of sodium diffusion and adsorption on boron-doped graphyne as promising anode material in sodium-ion batteries. Phys. Chem. Chem. Phys. 2018, 20, 29889−29895.

(32) Yang, Z.; Zheng, Y.; Li, W.; Zhang, J. Investigation of two-dimensional hf-based MXenes as the anode materials for li/na-ion batteries: A DFT study. J. Comput. Chem. 2019, 40, 1352−1359.

(33) Bhuvaneswari, R.; Nagarajan, V.; Chandiramouli, R. Investigation on bare and hydrogenated Sb-nanosheets as an electrode material for Na-ion battery-A DFT study. Phys. B 2019, 562, 75−81.

(34) Sun, C.; Searles, D. J. Lithium storage on graphdiyne predicted by DFT calculations. J. Phys. Chem. C 2012, 116, 26222−26226.

(35) Jia, Z.; Li, Y.; Zuo, Z.; Liu, H.; Huang, C.; Li, Y. Synthesis and Properties of 2D Carbon-Graphdiyne. Acc. Chem. Res. 2017, 50, 2470−2478.

(36) Huang, C.; Li, Y.; Wang, N.; Xue, Y.; Zuo, Z.; Liu, H.; Li, Y. Progress in research into 2D graphdiyne-based materials. Chem. Rev. 2018, 118, 7744−7803.

(37) Li, G.; Li, Y.; Liu, H.; Guo, Y.; Li, Y.; Zhu, D. Architecture of graphdiyne nanoscale films. Chem. Commun. 2010, 46, 3256−3258.

(38) Shang, H.; Zuo, Z.; Li, L.; Wang, F.; Liu, H.; Li, Y.; Li, Y. Ultrathin graphdiyne nanosheets grown in situ on copper nanowires and their performance as lithium-ion battery anodes. Angew. Chem., Int. Ed. 2018, 57, 774−778.

(39) Haley, M. M.; Brand, S. C.; Pak, J. J. Carbon networks based on dehydrobenzoannulenes: synthesis of graphdiyne substructures. Angew. Chem., Int. Ed. 1997, 36, 836−838.

(40) Chang, F.; Huang, L.; Li, Y.; Guo, C.; Diao, Q. A short review of synthesis of graphdiyne and its potential applications. Int. J. Electrochem. Sci. 2017, 12, 10348−10358.

(41) Wang, W. B.; Brand, S. C.; Pak, J. J.; Haley, M. M. Synthesis of expanded graphdiyne substructures. Chem. - Eur. J. 2000, 6, 2044−2052.

(42) Xu, Z.; Lv, X.; Li, J.; Chen, J.; Liu, Q. A promising anode material for sodium-ion battery with high capacity and high diffusion ability: graphyne and graphdiyne. RSC Adv. 2016, 6, 25594−25600.

(43) Mortazavi, B.; Shahrorkhi, M.; Zhuang, X.; Rabczuk, T. Boron−graphdiyne: a superstretchable semiconductor with low thermal conductivity and ultrahigh capacity for Li, Na and Ca ion storage. J. Mater. Chem. A 2016, 4, 11022−11036.

(44) Muhammad, I.; Wang, S.; Liu, J.; Xie, H.; Sun, Q. Boron-graphdiyne as an anode material for Li, Na, and K ion batteries with high capacities and low diffusion barriers. J. Renewable Sustainable Energy 2019, 11, No. 014106.

(45) Narita, N.; Nagai, S.; Suzuki, S.; Nakao, K. Optimized geometries and electronic structures of graphyne and its family. Phys. Rev. B 1998, 58, 11009−11014.