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A promising anode material for sodium-ion battery with high capacity and high diffusion ability:
Graphyne and Graphdiyne

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Investigation for energetics and dynamics properties of sodium adsorption on the graphyne and graphdiyne have been carried out by the first-principles calculations. Graphyne (GY) and graphdiyne (GDY) is the single atomic layer structure of the carbon six-member rings connected by one and two acetylenic linkages, respectively. Our calculated results indicate that a novel atomic hollow structure of graphyne and graphdiyne made up of sp- and sp²-hybridized carbon atoms reinforces not only the Na storage capacity but also the Na diffusion. For GY and GDY, the maximum sodium storage concentration is NaC$_{12}$ and being also superior to that case of Li inserting into graphite to form LiC$_{6}$. Only overcoming smaller energy barrier of about 0.4eV, Na ions can easily achieve two-dimensional diffusion on the GY and GDY plane. Excellent performances of sodium storage capacity and sodium diffusion ability make graphyne and graphdiyne promising candidates for the anode material used in sodium-ion battery.
monolayer GY and GDY can be as high as 558 and 744 mAh/g (LiC\textsubscript{6} and LiC\textsubscript{6}O\textsubscript{2})\textsuperscript{37, 38, 41}, respectively, which is twice that of the commercial graphite system (372 mAh/g, LiC\textsubscript{6})\textsuperscript{25, 26, 43-46}. On the other hand, experimental works for lithium storage in graphite (GY) have been successfully carried out\textsuperscript{6, 47}, and experimental results show outstanding performances of high capacity 520 mAh/g after 400 cycles and long cycle lives for lithium storage in graphite. All these evidences demonstrate a fact that GY and GDY is the promising candidate anode material for next generation lithium-ion batteries (LIBs).

Inspired by previous works of pursuing GY and GDY as the excellent anode material for lithium-ion batteries (LIBs), a question hanging on our heads that whether it is possible to applying GY and GDY to the fields of sodium-ion batteries (SIBs). To the best of our knowledge, to date, hardly any experimental effort of research on sodium storage on GY and GDY has been reported, even for theoretical calculation. To provide guidance for future experimental works, in this paper, we have firstly performed the first-principles calculations to pore the energetics and dynamics of sodium in GY and GDY.

2. Methods and computational details

As we know DFT hardly gives correct description for the interlayer Pack methods\textsuperscript{4, 48}. So our calculations for energetics and dynamics of sodium in GY and GDY were based on the dispersion-correlated density functional theory (DFT-D\textsuperscript{49, 50}) provided by the CASTEP code\textsuperscript{51}. According to the recommendation that DFT-D including the vdW weak interactions can be competent for the vdW interaction on the bonding of Li-GDY and Li-diffusion\textsuperscript{52}. Li and Na is the kin element with a certain similarity. Therefore, in this work, Grimme’s DFT-D2\textsuperscript{53} approach\textsuperscript{54} was applied to describe the weak interactions of carbon layers. PBE\textsuperscript{55} exchange function of GGA was chosen for our calculations and ultrasoft pseudo potentials (USPP)\textsuperscript{56} introduced by Vanderbilt\textsuperscript{57} was employed for all the ion–electron interactions. Here, C 2s\textsuperscript{2}2p\textsuperscript{2} electrons and Na 2p\textsuperscript{6}3s\textsuperscript{1} electrons were explicitly regarded as the valence electrons. Convergence with respect to both energy cutoff and k-point mesh has been tested strictly. Considering convergence tests and computational efficiency comprehensively, an energy cutoff of 500 eV was chosen to ensure that the total energies were converged within 1×10\textsuperscript{-6} eV/atom. For the Brillouin zone sampling, we carried out 4×4×2 and 6×6×2 for GY and GDY by using the Monkhorst-Pack\textsuperscript{58}

In order to determine the most-stable configuration of Na-GY and Na-GDY models, atom and cell optimizations were performed beforehand by using the total energy minimization methods. The total-energy difference is within 10\textsuperscript{-6} eV/atom, the maximum force is within 0.01 eV/Å, the maximum stress is within 0.01 GPa and the maximum atom displacement is within 10\textsuperscript{-4} Å. Two-dimensional periodic boundary condition was introduced to the calculations for GY and GDY. Moreover, a vacuum region of 15 Å was also applied in the direction perpendicular to the GY and GDY plane to eliminate the interactions between adjacent configurations. For bulk GY and GDY, (2×2) supercells containing two GY and GDY layers with an AB stacking sequence were constructed. The stability of Na-GY and Na-GDY system can be estimated by their according sodium average adsorption energy (\(\Delta E\)). The average adsorption energies were calculated by the following equation\textsuperscript{59}: \(\Delta E = \left( \frac{E_{\text{Na-GY or GDY}} - (E_{\text{GY or GDY}} + E_{\text{Na}})}{n} \right)\). Here, \(E_{\text{Na-GY or GDY}}\), \(E_{\text{GY or GDY}}\) and \(E_{\text{Na}}\) is total energies of the Na-GY or Na-GDY system, the GY, GDY and Na in its pure bulk, respectively, \(n\) is the total number of Na atom in Na-GY or Na-GDY system.

3. Results and discussions

3.1 Na adsorption on GY and GDY

Firstly, we relaxed the (2×2) supercell for single-layer GY and GDY, as depicted in Figure 1. The optimized lattice constant \(a\) is 6.89 and 9.45 Å, respectively for single-layer GY and GDY, which is in good agreement with the results of 6.86 and 9.48 Å from other DFT calculations\textsuperscript{37, 41}. The average bond length between the sp\textsuperscript{2}-hybridized C atoms is 1.417 and 1.424 Å, respectively for single-layer GY and GDY, close to that in graphene. The average distance of C-C\textsuperscript{3hybridized} and Na\textsuperscript{2hybridized} in the middle of acetylenic triple bond is 1.217 and 1.227 Å, and C-C bond connecting sp- and sp\textsuperscript{2}-hybridized carbon atoms has an average length of 1.42 and 1.402 Å, respectively for single-layer GY and GDY. In addition, a special C(sp)\textsuperscript{2}-C(sp) triple bond is 1.217 and 1.227 Å, and C-C bond connecting sp- and sp\textsuperscript{2}-hybridized carbon atoms has an average length of 1.42 and 1.402 Å, respectively for single-layer GY and GDY.

Figure 1. Schematic plots for the single-layer graphyne (a) and graphdiyne (b) of a (2×2) supercell and possible Na adsorption sites

Then, we investigated one Na atom adsorption on single-layer GY and GDY. Referring to some previous analogous works, Li atoms preferentially adsorb over the center of hexagon and triangular-like pores (hollow sites) on GY and GDY planes\textsuperscript{33, 37, 39, 41}. Therefore, for GY, two typical hollow adsorption sites were considered: above the
A site is also excluded out the GY plane, with a lower adsorption A site, indicating the corner of triangular-like pore (C site) of GDY is 
indicate that for single-layer GY, the stable configuration for double-layer GY and GDY. The calculated results listed in Table 1 
calculated several cases of Na atoms adsorption on single and 
double-layer GY and GDY. The calculated results listed in Table 1 indicate that for single-layer GY, the stable configuration for maximum sodium storage is NaC$_6$, in which Na is located above the center of triangular-like pores (A site) with a lower average adsorption energy of 1.82 Å. While for case of double-layer GY with AB stacking pattern, the optimized Na-intercalated double-layer GY is depicted in Figure 2a, which responds to the maximum sodium storage configuration (NaC$_6$). Here, Na atoms are simultaneously located above the center of triangular-like pores (A site) and above the center of hexagons (B site) with a lower average adsorption energy of 1.96 Å and an average adsorption height of 1.92 Å. In addition, the distance of Na inserted double-layer GY increases only by 16% from 3.3 to 3.8 Å, indicating the structural stability of charge and discharge process.

For single-layer GY, it is found that every triangular-like pore can furthest store three Na atoms at three symmetric corners, making a unique Na occupation pattern called as a triangular pattern and the stable configuration for maximum sodium storage responds to NaC$_6$. The average adsorption energy for this occupation configuration was computed to be -1.3eV/Na, with an average adsorption height of 1.96 Å. For double-layer GY with AB stacking pattern, the configuration with maximum sodium storage capacity not losing structural stability corresponds to NaC$_{18}$, as depicted in Figure 2b. The distance of Na inserted double-layer GY increases by 20% from 3.5 to 4.2 Å. The corresponding average adsorption energy is -2.03 eV/Na, and average adsorption height is 2.03 Å. All these adsorption energies for several Na atoms adsorption on GY plane are far larger than the cohesive energy (0.149 eV) of Na bulk, indicating that the clustering of Na atoms could be avoidable since it is energetically prohibited. It is noteworthy that while three C sites (Figure 1b) of triangular-like pore in GY are fully occupied, these three Na atoms all extrude out of GY plane and separate from each other, which is different from that case of one Na adsorption in the center of GY plane. Our calculations explicitly verified that three Na adsorption above the double-layer GY plane forming NaC$_{18}$ is more favorable than the corresponding configuration (NaC$_6$) with three Na atoms located above the single-layer GY by 0.26 eV/Na. It is due to the stronger Coulomb attractive interactions between positively charged Na ions and negatively charged host layers, induced by substantial charge transfer from Na to GY plane for both hollow sites, as revealed by the Hirshfeld population analysis of Na losing average 0.38 and 0.29e, respectively for NaC$_6$ and NaC$_{18}$ system.

![Figure 2. Charge density of GY (a) and GDY (c) monolayers (in electrons/A$^3$), electrostatic potential projected on a slice containing](image-url)
both A and B sites and perpendicular to the single GY (b) and GDY (d) monolayers.

For the ionic bonded Na-GY and Na-GDY adsorption systems, the adsorption energy and adsorption height is the result of interaction balance of the electrostatic attraction between positively charged Na ions and negatively charged GY and GDY. host layer and the short-range electron repulsion among positive Na ions. Therefore, the A site is preferentially energetic for one Na (positively charged) adsorption than the B and C site. As evidence depicted in Figure 3, the plane plot of negative charge density of GY and GDY containing both A, B and C sites and the electrostatic potential slices perpendicular to GY and GDY plane can further confirm above viewpoints. Viewed from Figure 3a and 3c, we find the negative charges are mainly localized between the A, B and C sites and the electrostatic potential slices parallel to GY and GDY plane.

3.2 Na diffusion in GY

Considering the ability of Na migration plays a significant role in the electrochemical performance of Na-ion battery system, we subsequently investigated Na migration behaviors between the adjacent adsorption sites on GY and GDY monolayer. It is noteworthy that the following calculations for Na migration mainly focus on a single Na ion behavior. The transition-state searches for the Na ion migration paths and activation barriers were probed by the LST/QST method. For GY, two main diffusion paths were discussed, such as in-plane diffusion paths (B site to A site, and A site to A site) as depicted in Figure 4a. In addition, two out-plane diffusion paths across the hollow have been also studied (Figure 4b and 4c).

Figure 4. Schematic drawings of diffusion paths (bottom panel) and corresponding energy curves (middle panel) as a function of adsorption sites of Na on GY monolayers, and the corresponding transition states (TS) (top panel) are also demonstrated in (a). Energy curves for Na across the large triangle (b) and the small hexagon (c) of GY monolayers as a function of adsorption height. The energies of equilibrium adsorption configurations are all set to zero.

The calculated energy curves (Figure 4a) show that the transition state for diffusion path B to A is located on the top of midpoint of the Q(sσ)-Q(sσ) bond between two adjacent hollows of large triangle and small hexagon. To verify the accuracy of TS prediction using the LST/QST method, we have also calculated other reaction paths by means of starting from the TS and moving down toward the minima along both reactant and product directions. As expected, no energy minima was found on those paths other than the reactant and product. Na migration along the B to A direction has a small activation energy barrier of 0.18 eV. However, when Na diffuse in the reverse direction (A to B), this process responds to a relatively high energy barrier of about 0.83 eV, due to the energetic favorability for the A site over B site. The energy barrier for Na hoping between two neighbouring A sites was found to be 0.4 eV, lower than that in A to B diffusion path. This responds to the transition state located on the top of midpoint of the Q(sσ)-Q(sσ) triple bond between two adjacent large triangle hollows. Given the energetic stability and kinetics of Na-GY system, the in-plane Na migration on GY is mainly dominated by the A to A hoping path with a mezzo energy barrier of about 0.4eV, which is superior to that case of Li diffusion on GY with higher energy barriers of 1.53-0.57eV.

The rest of two out-plane diffusion paths for GY were also explored, in which Na ions migrate across the hollows from one side.
of a GY layer to another side along the direction perpendicular to the GY plane. To improve the computational efficiency without losing accuracy, in our calculations of energy profiles for Na out-plane diffusion, these carbon atoms nearest and second nearest to Na ions were allowed to move while the remaining carbon atoms were all kept fixed. Figure 4b and 4c show the energy profiles of two typical out-plane diffusion paths. The energy barrier for Na diffusion through a small carbon hexagon is as high as 27 eV. Such an extremely high energy barrier indicates that the out-plane diffusion for Na across a small carbon hexagon is strictly prohibited both in energetics and kinetics under normal working conditions. More interestingly, our calculated results reveal that Na can easily migrate through the large carbon triangle by overcoming a relatively larger energy barrier of 2.49 eV, much less than that Na diffusing through the small carbon hexagon of graphite, GY and graphene. Therefore, we can conclude that the large hollows resulted from the special sp²- and sp-hybridized carbon atoms in GY accelerate not only the Na adsorption but also the out-plane Na migration.

3.3 Na diffusion in GDY

For GDY, in view of the stable adsorption sites, five main diffusion paths were investigated, divided into four in-plane diffusion paths and one out-plane diffusion path, such as B to C, C to A, A to A, Q(1) to Q(1) and Q(1) to Q(2), as depicted in Figure 5a. Although C is not the stable adsorption sites for one Na atom, a unique stable Na occupation pattern on C sites can occur by three symmetric corners of the triangular-like hollows occupied with three Na atoms. Therefore, an important out-plane diffusion path Q(1) to Q(2) through the large carbon triangle has also been studied.

Viewed from the calculated energy profiles of Na diffusion on the GDY plane (Figure 5b), Na migration along the B to C direction has a small energy barrier of 0.175 eV, close to that case of B to A diffusion path with an energy barrier of 0.18 eV on the GY plane. The corresponding transition state is located above the C(sp²)-C(sp²) bond. While the energy for a Na diffusion in the C to A path is monotonous, consistent with that electrostatic potential plot (Figure 3d) and above conclusion of one Na preferentially adsorbing on the A site. Interestingly, the energy barrier for Na diffusion in the opposite direction (A to C to B) responds to a relatively high value of 1.089 eV, due to the energetic favorability for the A site over B site. There are two possible hoping patterns for Na migration between the adjacent triangular-like hollows of the GDY, A to A and C to C, which responds to the energy barrier of 0.64 and 0.39 eV (Figure 5c), respectively. For the out-plane Na diffusion, it has a relatively higher energy barrier of 4.5 eV, indicating that when all the corner of triangular-like hollows occupied by Na ions, Na diffusion through the large hollows from one side to another side of GDY layer is energetically prohibited. But it doesn’t hide away the excellent performance of Na diffusion in the plane of GDY. Given the energetic stability and kinetics of Na-GDY-system, the in-plane Na migration on GDY is mainly dominated by the A to A and C to C hopping paths with mezzo energy barriers of 0.39-0.64 eV, close to that case of Li diffusion in GDY with energy barriers of 0.35-0.52 eV

Figure 5. Schematic plots of diffusion paths (a) and corresponding energy curves as a function of adsorption sites of Na on GDY monolayers, and the corresponding transition states (TS). Energy curves (b) and (c) for Na diffusion between two adjacent adsorption sites in the GDY plane, (d) Na diffusion out the plane across the large triangle of GDY monolayers. Here, the minimum energies are all set to zero.

Conclusions

Energetics and dynamics properties of sodium on the graphene and graphyne have been investigated by the first-principles methods. Calculations indicate that the unique atomic hollow structure of graphene and graphyne resulted from the special sp²- and sp-hybridized carbon atoms accelerates not only the Na storage capacity but also the Na diffusion. Similar to the case of lithium storage in GY and GDY to form the ceiling compounds of LiC₃ and LiC₄, the stable configuration for maximum sodium storage capacity of GY and GDY also responds to NaC₃ and NaC₄, respectively, which far exceed that case of Na inserting into graphite to form stage-II ceiling compound NaC₂ and is also superior to that case of Li inserting into graphite to form LiC₂. Two-dimensional fast Na diffusion (in-plane) in the Na-GY and Na-GDY system can be implemented by overcoming smaller energy barrier of about 0.4 eV. The advantages of Na storage capacity and Na diffusion ability make graphene and graphyne promising candidates for the anode material in sodium-ion battery application.

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