Graphitic Carbon Nitride Nanotubes As Li-Ion Battery Materials: A First-Principles Study

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ABSTRACT: First-principles calculations based on density functional theory are carried out to investigate the Li storage capability of graphitic carbon nitride nanotubes. The porous nanotubes provide unprecedented opportunity for energy storage due to their uniform size of pores in the wall and doubly bonded nitrogen at the edges of the pore. The calculations predict that the Li atoms can easily access the interior of the nanotube through the pores in the wall because of the low energy barrier and thus be stored both inside and outside of the nanotubes. The exothermic intercalation of Li further shows that g-C$_3$N$_4$ nanotubes are suitable for Li storage. The Li density in bundles of nanotubes is predicted to be up to 0.37 (Li$_x$C$_3$N$_4$). The porous graphitic carbon nitride nanotubes are applicable in Li-ion battery with high density and stability.

I. INTRODUCTION

Sustainable alternative energy sources, including solar irradiation, wind, wave, and geothermal energy, have been widely pursued due to the limited supply of the old forms of depletable energy (coal, oil, and nuclear) and their detrimental effects on the global climate. However, these energy sources are variable in time, diffuse in space, or restricted in location. Definitely, electrical energy storage is essential and benefited to these energy sources. The portable chemical energy is the most convenient form for energy storage. A battery generally provides two functions: the ability to supply power over a duration of time and the ability to store the chemical energy with a high conversion efficiency and no gaseous exhaust. The battery is preferred to store the chemical energy converted from the alternative energy sources. Therefore, rechargeable batteries with high energy density are in great demand as energy sources for various purposes, e.g., portable electronic devices, zero emission electric vehicles, and load leveling in electric power. Lithium secondary batteries are the most promising to fulfill such needs because of their intrinsic discharge voltage with relatively lightweight and high capacity. The performance of batteries, including energy density, power density, cyclability, and safety, are required to be enhanced to satisfy the increasing needs of new applications. Extensive research has been focusing on designing new materials to improve the performance. Li-storage in nanostructured materials has been proved to be one of the most important strategies for the improvement of performance. The use of nanomaterial electrodes, especially one-dimension nanostructures, has led to huge improvement of performance compared with bulk materials and has been demonstrated with carbon nanotubes, silicon nanowires/nanotubes, and their composites. For example, Si nanowires showed a high charge/discharge capacity close to 75% of the theoretical value (4200 mAh/g). Further improvement of the capacity and stability, mesoporous Si/carbon core–shell nanowires with ordered separation were reported to have excellent lithium reactivity with a reversible capacity of 3163 mAh/g at a rate of 0.2 C. Although the research on Si-based Li-ion battery is very encouraging because of the high specific capacity, the Li-intercalation during lithiation leads to the volume’s change of 300% of Si and, accordingly, Si-based battery’s instability. Therefore, the study on the anode materials made from lightweight materials, such as carbon and carbon nitride, has attracted extensive attention because of their weight and stability. Theoretical and experimental studies have shown that the maximum Li storage capacity in carbon nanotubes (CNTs) can be increased up to LiC$_6$ (1250 mAh/g), much higher than that in graphite (372 mAh/g). Various compound nanotubes, such as SiC, BN, BC$_3$, and BC$_2$N, have been investigated as Li-ion anode materials. However, it is difficult for lithium to enter the interior of the perfect and capped nanotubes. To enhance Li-storage capacity in these nanotubes, chemical etching, ball-milling, and doping of the nanotubes have been used to create defects on their wall, open their ends, or introduce functional atoms to their outside wall or inside of the nanotubes. One of the efficient ways is to create pyridinelike defects on the tube’s wall, which help...
lithium penetrate into the tube’s interior. Recently, a novel porous nanotube, graphitic carbon nitride nanotube, was proposed for water splitting and hydrogen storage. This nanotube is obtained by rolling up the graphitic carbon nitride monolayer (Figure 1a). The first-principles calculations predicted that g-C$_3$N$_4$ nanotube with larger diameter is more stable than the sheet because of lower formation energy and should be possible to be fabricated under suitable experimental conditions. The geometry of g-C$_3$N$_4$ with the AB structure is the most stable phase of carbon nitride, which is a heptazine-based form (Figure 1a). It is expected that the Li storage in this nanotube should be greatly enhanced due to its porous structure and dangling states. In this work, the capacity of Li-ion battery based on the g-C$_3$N$_4$ nanotube is investigated. The electronic and structural properties of Li-intercalated g-C$_3$N$_4$ nanotube are studied by first-principles calculations. The Li intercalation energy is negative and the specific energy increases with increasing Li density up to 0.57. The g-C$_3$N$_4$ nanotube is predicted to be one of the important candidates for Li-ion battery.

II. METHODS

The first-principles calculation is carried out based on the density function theory and the Perdew–Burke–Eznerhof generalized gradient approximation (PBE-GGA). The projector augmented wave (PAW) scheme as incorporated in the Vienna ab initio simulation package (VASP) is used. The Monkhorst and Pack scheme of k-point sampling is used for integration over the first Brillouin zone. The most stable structure of carbon nitride is the graphitic phase, g-C$_3$N$_6$, which is a heptazine-based form (Figure 1a). The geometries of g-C$_3$N$_4$ with the AB structure and one g-C$_3$N$_4$ monolayer are first optimized to obtain the lattice constants. For monolayer, a vacuum space with 12 Å is used to minimize the interlayers interaction. A $5 \times 1 \times 1$ grid for k-point sampling and an energy cutoff of 400 eV are used for the bulk and monolayer. The g-C$_3$N$_4$ nanotubes are constructed by curling up one monolayer into a cylinder along x direction, labeled as g-C$_3$N$_4$-zzn, where zz is zigzag and n is the index ($n = 3–10$). A $1 \times 1 \times 3$ grid for k-point sampling and an energy cutoff of 400 eV are consistently used in our calculations on the g-C$_3$N$_4$ nanotubes. Good convergence is obtained using these parameters, and the total energy is converged to $2.0 \times 10^{-5}$ eV/atom, which is the self-consistent cycle convergence. A large supercell dimension with a wall–wall distance of 10 Å in the plane perpendicular to the tube axis is used to avoid interaction between the nanotube and its images in neighboring cells. The computational parameters are carefully examined against the convergence. The estimated error is less than 1 meV, which is negligible when comparing with calculated binding energy (up to 2 eV) as discussed in the following section. The van der Waals interaction is not considered in our calculations.

III. RESULTS AND DISCUSSION

The calculated distance between two pores and interlayer distance in the AB g-C$_3$N$_4$ are 7.133 and 3.543 Å, respectively, consistent with the literature. The in-plane repeat period of the g-C$_3$N$_4$ nanotube in the x direction is 7.129 Å, slightly smaller than that of its corresponding bulk. The heptazine structures in the optimized geometries of g-C$_3$N$_4$-zz remain almost as flat as in the monolayer after the optimization. The C–N–C angle ($\theta$) at the heptazine–heptazine N connection (Figure 1a) is reduced to 106°, leading to large local curvature. However, the lattice distortion both in the heptazine and at the connection is less than 0.5%. To give an example on the geometries of the g-C$_3$N$_4$ nanotubes intercalated with Li, we first show the optimized nanotube with one Li atom (Figures 1b,c), where g-C$_3$N$_4$-zz6 is used and one Li atom is put at the center of pore in the nanotube in the supercell because the pore site is energetically more preferable for Li adsorption. The optimized geometry of the Li-intercalated tube is very similar to that of pure g-C$_3$N$_4$ nanotube and the Li-intercalation has a negligible effect on the tube’s geometry, indicating that the diffusion of Li in the g-C$_3$N$_4$ nanotubes should be easy. Normally, the energy barrier of Li diffusion is defined as the energy to be overcome for Li atom moving from one energy minimum to another. For perfect nanotubes, such as CNT and BC$_3$, Li atoms prefer to stay away from the nanotube’s wall (energy minimum). The Li diffusion from exterior to interior through a hexagon (nanotube’s wall) should overcome high energy barrier (energy maximum). For g-C$_3$N$_4$ nanotube, the pore site holds Li atoms at energy minimum. The calculated energy profile (see Figure S1, Supporting Information) shows that Li atom can move freely (no barrier) from the exterior of g-C$_3$N$_4$ nanotube to its pore. To move into its interior, Li atom needs to overcome the adsorption energy at the pore. Therefore, we define the energy barrier as the adsorption energy difference between one internal site and the pore center. We see that the energy barrier is dependent on Li position within the nanotube. The energy barrier increases with Li moving to the nanotube’s center. The calculated maximum energy barrier for Li penetrating from the pore into the center of the g-C$_3$N$_4$ nanotube is about 1.8 eV, which is much less than those for

![Figure 1. Structure of graphitic carbon nitride (g-C$_3$N$_4$) monolayer (a); top view (b) and (c) side view of g-C$_3$N$_4$ nanotube with a Li atom at the center of the pore.](image-url)
carbon (10.5 eV) and BC₃ (4.6 eV) nanotubes, but slightly larger than that of the CNTs with the pyridinelike defect although the size of the pore in g-C₃N₄ tube is larger than that of the pyridinelike defect in CNTs. The calculated diffusion energy profile of Li atom in g-C₃N₄ nanotube clearly shows that Li atoms more easily attach to the nanotubes wall due to negative adsorption energy, while they should stay away from the wall of CNT/BC₃ nanotube because of positive energy. The relatively negative adsorption energy and lower energy barrier indicate that the diffusion of Li into the porous nanotube is much easier.

To investigate the effect of Li-intercalation on the electronic property of the nanotube, the electronic structure of the nanotube with Li atom is calculated (Figure 2). The pure nanotube is a semiconductor with a gap of 1.72 eV. The nanotube intercalated with one Li atom in the supercell is an n-type semiconductor because of the charge transfer from Li to nanotube (∼0.2 e, estimated from Mulliken population analysis) (Figure 2a), as demonstrated by the Fermi level within the conduction band. The analysis on partial density of states (PDOS) reveals that the valence band bottom (VBT) and conduction band top (CBT) are mainly attributed to the p electrons from N atoms at the edge (N₁ in Figure 1a) and center (N₂ in Figure 1a), and the p electrons from C atom at the connection (C₂ in Figure 1a) and N atom at the center (N₂ in Figure 1a), respectively (Figure 2b).

To further investigate the Li-storage capacity of the g-C₃N₄ nanotubes, we study the intercalation density by putting various densities of lithium atoms at both the outside and inside of the tubes, and the size effect on the capacity. At low intercalating density, the Li atoms prefer to occupy the pores on the nanotube. Each pore can hold up to three Li atoms with one Li close to two doubly bonded nitrogen atoms (N₁ in Figure 1a). Two of them stay slightly outside of the tube, and one inside. The Li–N bond length is about 1.96 Å. The distance between two outside Li atoms is 2.94 Å, which is comparable with that in Li bulk (2.97 Å) and indicates that Li-ion can be discharged (similar to bulk Li), and the distance between one outside Li and one inside Li is about 2.74 Å. The Li-intercalation at the pore has negligible effect on the structure distortion of the nanotube, which keeps almost unchanged. The calculated electronic property shows that the nanotube with every pore occupied by three Li atoms is metallic, as indicated by the Fermi level within the deep conduction band (Figure 3a). An additional band within the band gap is attributed to the p electrons from carbon and nitrogen atom (C₁, C₂, and N₂ in Figure 1a) (Figure 3b).

Figure 2. Calculated band structure (a) and partial density state (b) of g-C₃N₄ nanotube with a Li atom at the center of the pore.

Figure 3. Calculated total density of states (a) and partial density state (b) of g-C₃N₄ nanotube with every pore occupied by three Li atoms.

Figure 4. Top view (b) and (c) side view of g-C₃N₄ nanotube with the Li density at 0.48.

A number of electrochemical properties can be derived directly from the difference in total energies before and after lithium intercalation, a procedure offering improved accuracy through the cancellation of errors. The intercalation energy (E₁ₙₑₓ), as an indication for the stable storage of Li, is calculated from

\[ E_{\text{int}} = (E_{\text{tot}}(\text{tube} + n\text{Li}) - E_{\text{tot}}(\text{tube}) - n\mu_{\text{Li}})/n \]
where $E_{\text{tot}}(\text{tube + Li})$ and $E_{\text{tot}}(\text{tube})$ are total energies of the g-C$_3$N$_4$ nanotube with and without Li, respectively. $\mu_{\text{Li}}$ is the chemical potential of lithium calculated from the Li bulk. $n$ is the number of Li atoms or the Li density. The negative energy ($E_{\text{int}} < 0$) corresponds to exothermic chemical intercalation, leading to stable dissociation of Li bulk and separation of Li atoms in the g-C$_3$N$_4$ nanotubes; while the positive energy ($E_{\text{int}} > 0$) relates to the endothermic reaction, resulting in thermodynamically unstable intercalation. The Li-intercalation energy in g-C$_3$N$_4$ nanotubes depends on the tube’s size and the density of Li, as shown in Figure 5. In the case of every pore in g-C$_3$N$_4$ nanotube intercalated with one Li atom, the intercalation energy decreases and converges to $-1.86$ eV with the increase of the diameter, although there is a maximum at the tube’s diameter of about 9 Å (g-C$_3$N$_4$-zz4) (Figure 5a), indicating that the nanotubes with larger diameter are more suitable for Li storage. The energy slightly increases with the increase of the diameter when every pore holds three Li atoms, but the fluctuation is within 0.05 eV (Figure 5b). The results on the intercalation energy for the smaller g-C$_3$N$_4$ nanotubes (g-C$_3$N$_4$-zz3 and g-C$_3$N$_4$-zz4) with three Li atoms per pore are not included in Figure 5a because the intercalated nanotubes are strongly distorted after geometry relaxation due to the strong Li–Li interaction. The exothermic intercalation indicates that larger g-C$_3$N$_4$ nanotubes are suitable for Li storage.

To predict the highest intercalation density of Li in g-C$_3$N$_4$ nanotubes, we calculate the specific energy of g-C$_3$N$_4$-zz6 with the intercalation density up to Li$_{3.5}$g-C$_3$N$_4$. The specific energy ($E_{\text{s}}$) is given by ref 52

$$E_{\text{s}} = -(E_{\text{tot}}(\text{tube} + n\text{Li}) - E_{\text{tot}}(\text{tube}))/m$$

where $E_{\text{tot}}(\text{tube} + Li)$ and $E_{\text{tot}}(\text{tube})$ are total energies of the g-C$_3$N$_4$ nanotube with and without Li, respectively. $m$ is the total number of carbon and nitrogen atoms in the supercell. The intercalation density ($D_i$) is the number of Li atoms in the supercell divided by $m$. We find that the specific energy increases with the intercalation density (Figure 6), indicating that the $D_i$ might be as high as 0.5 in a single nanotube. The specific energy at an intercalation density of 0.48 is 1.1 eV (Figure 6). The calculated intercalation energy increases with the increase of intercalation density (inset in Figure 6), but converges to $-0.25$ eV at the Li density up to 0.5. Importantly, the intercalation energy is negative in the whole range of the considered intercalation density, indicating that the reaction is exothermic. The calculated specific and intercalation energies show that the $D_i$ should be higher than 0.5 in tube bundles because of the spacing in the bundles. We further study the Li storage in a bundle of g-C$_3$N$_4$ nanotubes. The calculated specific and intercalation energies in a bundle of g-C$_3$N$_4$-zz6 with a Li density at Li$_4$g-C$_3$N$_4$ ($D_i = 0.57$) are 1.22 and $-0.23$ eV, respectively (Figure 7). Compared with these in a single nanotube, where the specific energy is increased, the specific energy is still negative and only increased by 0.02 eV, indicating the bundle can host more Li atoms. We can see that the Li storage in g-C$_3$N$_4$ nanotubes is higher than that in graphite and comparable with or even higher than that in carbon nanotubes.4

Figure 5. Calculated intercalation energies for the g-C$_3$N$_4$ nanotubes with (a) one Li atom and (b) three Li atoms per pore as a function of diameter.

Figure 6. Calculated specific energy as a function of Li density. The inset shows the intercalation energy as a function of Li density.

Figure 7. Structure of graphitic carbon nitride (g-C$_3$N$_4$) nanotube bundle with filled Li atoms.
Experimentally, the electrochemical testing showed that bulky g-C₃N₄ had a low intercalation capacity and poor stability because Li reacted with a C3N species on the g-C₃N₄ sheet, which destroyed the crystallinity of g-C₃N₄.53,54 Our calculations show that Li atoms prefer to be adsorbed to the pore’s edge (C₂N₄ species), which are stable for Li-intercalation.54 The relaxed geometry of Li-adsorbed g-C₃N₄ nanotube clearly shows that the lithiation has little effects on the geometrical structure (Figure 7). Therefore, the g-C₃N₄ nanotubes may show better performance on capacity and stability.

IV. CONCLUSIONS

In summary, a porous graphitic carbon nitride nanotube is investigated for its application into Li storage by first-principles calculations. The porous nanotube offers more opportunities for the Li atoms to access its interior and store Li atoms both inside and outside of the porous nanotube, resulting in high intercalation capacity. The energy barrier for Li atoms to enter the interior of g-C₃N₄ nanotube is much lower than those of other nanotubes because of its porous structure. Although the intercalation energy initially increases with the increase of Li density, it converges to ~0.23 eV at the Li density up to 0.57, and the intercalation reaction is exothermic. The specific energy increases with the increase of the Li density and has not reached the maximum with Li density up to 0.57. These calculated results predict that the g-C₃N₄ nanotubes should have high potential as electrode materials for Li battery with better performance, high stability, and fast response.

ASSOCIATED CONTENT

Supporting Information
Calculated energy profile for Li atom diffusion from the nanotube’s exterior to its interior. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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