Graphyne Nanotubes as Promising Sodium-Ion Battery Anodes

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Abstract: Sodium-ion batteries (SIBs) are promising candidates for the replacement of lithium-ion batteries (LIBs) because of sodium’s abundant reserves and the lower cost of sodium compared to lithium. This is a topic of interest for developing novel anodes with high storage capacity. Owing to their low cost, high stability, and conductivity, carbon-based materials have been studied extensively. However, sp2-C based carbon materials have low-rate capacities. Intensive density functional theory calculations have been implemented to explore the applicability of α-GyNTs, β-GyNTs, and γ-GyNTs, respectively, as SIB anodes. Results suggest that (3, 0)-α-GyNT, (2, 2)-β-GyNT, and (4, 0)-γ-GyNT have, respectively, maximum Na storage capacities of 1535, 1302, and 1001 mAh/g, which exceeds the largest reported value of carbon materials (N-doped graphene foams with 852.6 mAh/g capacity). It was determined that α-GyNTs have the largest storage capacity of the three types because they possess the largest specific surface area. Moreover, the larger pores of α-GyNTs and β-GyNTs allow easier diffusion and penetration of Na atoms compared to those of γ-GyNTs, which could result in better rate capacity.

Keywords: graphyne; secondary battery; DFT; curvature effect

1. Introduction

The large-scale use of renewable energies would not only solve the urgent need to alleviate energy shortages, but also reduce the emissions of greenhouse gases in the push toward carbon neutrality [1]. To maximize the utilization of renewable energies, convenient and efficient storage equipment is essential [2]. Electrochemical batteries often play this important role due to their high stability and efficiency. Lithium-ion batteries (LIBs), first proposed by M.S. Whittingham in the 1970s [3], are a well-developed technology that has been applied widely in various fields [4,5]. Although LIBs can provide ultra-high specific capacity and energy density, lithium has limited abundance and is distributed non-uniformly within the earth’s crust. In the future, the demand for green energy equipment will increase rapidly, leading to rising costs of LIBs [6]. Therefore, it is imperative to find alternatives to lithium.

When compared to the rare, light metal lithium, sodium is distributed widely on land and in the sea in the form of salt, and is of much lower cost than Li [7]. Though differences in radius and mass affect the capacity and transportation properties [8], sodium and lithium are both alkali metals, and are close in the periodic table of elements, resulting in similar properties. Thus, sodium has been regarded as the most promising alternative for replacing Li in new generations of secondary batteries, which has become a high priority in the past decade [9]. Currently, the materials that have been applied for SIB anodes include: sodium metal [10,11], carbon-based materials [12,13], alloys [14], organic electrodes [15],...
and composites [16,17]. Although the specific capacity of sodium metal as SIB anodes can be comparable to that of LIBs [18,19], sodium metal anodes have limited large-scale applicability due to the safety concerns caused by dendrites. Though having large storage capacities, other elements of group 14 and 15, such as Si, Sn, P etc., suffer from major volume changes and other shortcomings [20,21]. When compared to other materials, carbon-based materials have received more widespread attention due to their low-cost, high structural stability, and flexibility [22,23]. Specifically, the large surface area and high electronic conductivity are important for inhibiting the formation of dendrites [24,25]. Many carbon materials, including graphite [26], hard carbon [27], hollow carbon nanospheres [28], and graphene [29], have demonstrated feasibility and potential as SIB anode materials. Note that the N-doped graphene foams synthesized by Dai’s group in 2015 was reported to have the largest storage capacity (852.6 mAh/g) up to now [30]. This work strongly demonstrates the well-defined carbon materials could have competing capacity to the LIBs. However, some shortcomings, especially with the small benzene rings in sp² carbon, can induce poor rate capacities [31]. In view of these efforts, development of a carbon material with large holes and large specific surface area has become key to solving these issues.

In 1987, Baughman et al. predicted a two-dimensional material with both sp- and sp²-hybridized carbon atoms, which was named graphyne (Gy) [32]. Li’s group first realized the synthesis of large-scale graphdiyne in 2010 [33]. Gy has abundant carbon chemical bonds, large conjugated systems, wide interplanar spacing, and excellent chemical stability. In the past decade, graphyne has become a hot issue in many application fields [34,35]. Especially in the field of ion batteries, where graphyne exhibits several advantages, including high specific capacity, excellent rate performance, and stability [36,37]. Recently, graphyne materials have received growing attention as potential SIB anodes. In 2017, Huang et al. reported a three-dimensional graphdiyne nanosheet as anode materials, which delivers a stable reversible capacity of 812 mAh/g at a current density of 0.05 A/g [38]. In 2019, they further reported well-defined hydrogen-substituted graphyne (HsGY) with a reversible capacity of 600 mAh/g at a current density of 100 mA/g [37]. In 2020, Cui’s group synthesized N-doped γ-graphyne (NGY) to deliver a large reversible storage capacity of 570.4 mAh/g at 100 mA/g, accompanied by excellent rate capability [39]. Through a first principles investigation, Xu et al. determined that graphyne and graphdiyne have not only high Na storage capacity, but also strong diffusions because of the existence of large sized pores [40]. These studies have demonstrated graphyne-related materials as potential SIB anode materials.

Formation of graphyne nanotubes (GyNTs) is one of many modification methods of graphyne. At present, many studies have confirmed that rolling 2D graphyne into nanotubes can significantly modify their structural and electronic properties [23,41,42]. We have reported that γGyNTs could be promising LIB anode materials as they have a predicted maximum lithium storage capacity of 2232 mAh/g [41]. It was discovered that the curvature of γGyNTs has great influence on the storage and migration of lithium. Thus, we believe GyNTs are promising candidates for next-generation SIB anode materials due to their large, conjugated, structure-adjustable curvature, and larger number of possible active sites. In addition, many graphyne-based materials including graphdiyne nanoribbons [42] and graphdiyne nanotubes [43] have been successfully synthesized, which makes us expect the realization of GyNTs in near future. Therefore, in the present study, we investigate the performance of GyNTs as SIB anode materials through density functional theory calculations. We calculate the maximum Na storage specific capacity of GyNTs with different radii and obtained the maximum specific capacities using binding energies, open circuit voltages, and structural characteristics. Our results show that all studied GyNTs have better maximum specific capacities than a single-layer Gy. Specifically, (3, 0)-αGyNT, (2, 2)-βGyNT, and (4, 0)-γGyNT, were predicted to have the best storage capacities of each type of graphyne, with values of 1535, 1302, and 1001 mAh/g, respectively. Our results further suggest that large hexagonal pores could resolve the transportation problem caused by the large atomic radius of sodium.
2. Computational Method

In this study, all density functional theory (DFT) calculations were implemented by the Vienna Ab Initio Simulation Package (VASP) with a projector-augmented wave (PAW) method [44]. The exchange–correlation functional was used with the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) scheme [45], coupling with spin polarization. The cutoff energy was set to 400 eV, and the geometries were optimized until no residual force acting on any atom exceeded 0.05 eV/Å, and the energy change was less than $10^{-4}$ eV. We applied each unit cell of the $\alpha$, $\beta$ and $\gamma$ GyNTs as a substrate to adsorb Na. The first Brillouin zone integration was conducted using the Monkhorst–Pack scheme with a $k$-point sampling of $1 \times 1 \times 4$ [46], where the $c$ axis was set as the periodic direction. The optimal structures of all studied GyNTs are available in the electronic supplementary information (ESI, Figures S1–S3). Therefore, we can determine the diffusion paths and diffusion energy barriers of Na atoms on GyNTs using the climbing-image-nudged-elastic-band (CI-NEB) [47].

The adsorption strength can be indicated by the binding energy ($E_b$) of Na atoms on every GyNT, which is defined below:

$$E_b = (E_{C-Na} - E_C - N E_{Na}) / N$$

where $N$ is the total number of Na atoms adsorbed on the GyNT, $E_{C-Na}$ is the total energy of Na atom(s) adsorbed on the GyNT, $E_C$ is the energy of the substrate GyNT, and $E_{Na}$ is the energy of an isolated Na atom in a vacuum.

To obtain the open-circuit voltage ($V_{OCV}$) of the SIB anode materials, the following formula can be applied [36]:

$$V_{OCV} = -\frac{\Delta G}{\Delta N e}$$

where $\Delta G$ is the difference in Gibbs free energy, $\Delta N$ is the difference in the number of Na ions at two compositions during charging/discharging, and $e$ is the electronic charge of the Na ions ($e = 1$).

$$\Delta G = \Delta E + P \Delta V - T \Delta S$$

because the contribution of the volume and entropy terms are negligible, $\Delta G$ can be approximated as $\Delta E$ [48]. Therefore, $V_{OCV}$ can be simplified to the following formula:

$$V_{OCV} = (E_C + N E_{bcc-Na} - E_{C-Na}) / \Delta N e$$

where $E_{bcc-Na}$ is the energy of one Na atom in body-centered cubic (bcc) form. The $E_b$ and $V_{OCV}$ of Na atoms adsorbed on a GyNT were calculated as a function of Na concentration $x$, where $x$ is defined from $C_6Na_x$. Taking $(3, 0)$-$\alpha$ GyNT for instance, $N = 8x$, so that $C_{48}Na_N$ is reduced to $C_6Na_x$.

3. Results and Discussion

3.1. Single Na Adsorption on GyNTs

First, we studied the adsorption of a single Na atom on 2D graphyne films. For $\alpha$ Gy, the single Na atom prefers to be adsorbed at the center of the hexagonal acetylenic ring ($H_\alpha$), as shown in Figure 1a. The distance between the Na and the sp-C atom ($R_{C-Na}$) is about 2.70 Å, and the $E_b$ was computed to be $-2.02$ eV by Equation 1. In contrast, $\beta$ Gy has two sites that anchor the Na atom, the centers of the hexagonal acetylenic ring, and the triangular acetylenic ring (denoted as $H_\beta$ and $h_\beta$, respectively). The optimized structures at $H_\beta$ and $h_\beta$ are presented in Figure 1b, which shows $R_{C-Na}$ values of 2.69 Å and 2.64 Å, with $E_b$ values of $-2.25$ and $-2.30$ eV, respectively. Similarly, $\gamma$ Gy also has two Na sites: the centers of hexagonal acetylenic ring and benzene ring (denoted as $H_\gamma$ and $h_\gamma$, respectively). The $E_b$ values at $H_\gamma$ and $h_\gamma$ were computed to be $-2.08$ and $-1.45$ eV, respectively. The $E_b$ at $H_\gamma$ is more negative than that at $h_\gamma$ because of its larger size, as shown in Figure 1c. Our results, consistent with the previous results of Xu et al. [40], indicate that the three
Gy models can anchor a Na atom because the cohesive energy ($E_{\text{coh}}$) of bulk Na is only $-1.04$ eV.

![Figure 1. Optimized structures of a single Na atom adsorbed in 2D (a) $\alpha$Gy, (b) $\beta$Gy, and (c) $\gamma$Gy.](image)

Next, we explored the adsorption of a single Na on GyNTs. Our previous work suggested that curvature can cause differentiations of sp- and sp$^2$-C atoms [41], inducing more possible adsorption sites. These sites include the top site (t) on single C atoms, the bridge site (b) between two bonded C atoms, and the hollow sites of acetylenic rings (denoted H or h depending on pore size), as illustrated in Figure 2. We used the superscript (') to represent concave cases. A Na atom was placed at these positions at initial distances (denoted H or h depending on pore size), as illustrated in Figure 2. We used the superscript (') to represent concave cases. A Na atom was placed at these positions at initial distances (denoted H or h depending on pore size), as illustrated in Figure 2. We used the superscript (') to represent concave cases. A Na atom was placed at these positions at initial distances (denoted H or h depending on pore size), as illustrated in Figure 2. 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3.2. Sodium Storage Capacity of GyNTs

In order to explore the maximum storage capacity, we gradually introduced more Na atoms into single-layered Gy films and GyNTs. The changes to $E_b$ and $V_{OCV}$ were computed as a function of Na concentration $x$, which was set as 0 when only a single Na atom was introduced.
considered for simplicity. Figure 4 shows the changes to $E_b$ and $V_{OCV}$ as a function of Na concentration $x$. The $C_{Na}^{\text{max}}$ values of 2D $\alpha\text{Gy}$, $\beta\text{Gy}$, and $\gamma\text{Gy}$ were determined to be $C_{6}\text{Na}_{1.5}$, $C_{6}\text{Na}_{1.0}$, and $C_{6}\text{Na}_{1.5}$. When reaching the $C_{Na}^{\text{max}}$ the corresponding $E_b$ values were $-1.35$, $-1.08$, and $-1.56 \text{ eV/Na}$, and the $V_{OCV}$ values were 0.014, 0.29 and 0.49 V by Equation 4 as shown in Figure 4. The optimized structures shown in Figure S4 indicate that all Na atoms are anchored and stable since all $R_{C-Na}$ are about 2.7 Å. Therefore, the maximum specific capacities of $\alpha\text{Gy}$, $\beta\text{Gy}$, and $\gamma\text{Gy}$, are 558, 372, and 558 mAh/g, respectively. It is notable that a previous study reported the maximum specific capacity of $\gamma\text{Gy}$ to be 558 mAh/g [40], which is consistent with our results, indicating the reliability of our calculations.

![Figure 4](image-url)

**Figure 4.** The changes to $E_b$ of (a) $\alpha$, (b) $\beta$, and (c) $\gamma\text{GyNTs}$ as a function of the Na concentration $x$, and $V_{OCV}$ as a function of Na concentration $x$ of (d) $\alpha$, (e) $\beta$, and (f) $\gamma\text{GyNTs}$.

When the 2D Gy is curled seamlessly into a GyNT, the $C_{Na}^{\text{max}}$ changes significantly, as revealed in prior work. The changes to $E_b$ and $V_{OCV}$ as a function of the Na concentration $x$ of $\alpha\text{GyNTs}$ are shown in Figure 4a,d. For $(n$, $n)$-$\alpha\text{GyNTs}$, the $C_{Na}^{\text{max}}$ values were computed to be $C_{6}\text{Na}_{3.94}$, $C_{6}\text{Na}_{3.50}$, and $C_{6}\text{Na}_{3.00}$ when $n = 2, 3$, and 4, respectively, and the corresponding $E_b$ and $V_{OCV}$ values are $-1.15$, $-1.19$, and $-1.22 \text{ eV/Na}$ and 0.12, 0.11, and 0.10 V, respectively. For $(n$, 0)$-$\alpha\text{GyNTs}$, the predicted $C_{Na}^{\text{max}}$ values are $C_{6}\text{Na}_{4.13}$, $C_{6}\text{Na}_{3.75}$, and $C_{6}\text{Na}_{3.53}$ when $n = 3, 4$, and 5, and their corresponding $E_b$ and $V_{OCV}$ values were $-1.17$, $-1.19$, and $-1.19 \text{ eV/Na}$ and 0.08, 0.11, and 0.09 V, respectively. To confirm the maximum sodium storage capacity of $\alpha\text{GyNTs}$, we checked the optimized structure of $(3$, 0)$-$\alpha\text{GyNT}$ with $C_{Na}^{\text{max}}$ as shown in Figure 5a, while the data for other $\alpha\text{GyNTs}$ are available in Figure S5. We discovered that every Na atom directly interacts with the C atoms of $\alpha\text{GyNTs}$. Therefore, the maximum Na storage capacity of $\alpha\text{GyNTs}$ is $C_{6}\text{Na}_{4.125}$ (1535 mAh·g$^{-1}$).
Following the same approach, we tried to determine the $C_{Na}^{max}$ values of the studied $\beta$GyNTs. The changes of $E_b$ and $V_{OCV}$ as functions of the Na concentration $x$ of $\beta$GyNTs is shown in Figure 4b,e. For $(n, n)-\beta$GyNTs, the expected $C_{Na}^{max}$ values are $C_{6Na_{2.25}}, C_{6Na_{2.94}},$ and $C_{6Na_{2.88}}$ when $n = 2, 3,$ and $4$, respectively, and the $E_b$ and $V_{OCV}$ values are $−1.18$, $−1.17$ eV/Na and $0.12, 0.11,$ and $0.10$ V, respectively, when the GyNTs reach the expected maximum storage capacity. For $(n, 0)-\beta$GyNTs, the expected $C_{Na}^{max}$ are $C_{6Na_{3.50}}, C_{6Na_{3.39}},$ and $C_{6Na_{3.08}}$ when $n = 2, 3,$ and $4$, respectively. The corresponding $E_b$ and $V_{OCV}$ values are $−1.15, −1.18,$ and $−1.16$ eV/Na and $0.08, 0.11,$ and $0.09$ V for the $(n, 0)-\beta$GyNTs. Moreover, we also checked the optimized geometries with the maximum storage capacity of $\beta$GyNTs, as shown in Figure 5b and Figure S6. Thus, the maximum storage Na capacity of $\beta$GyNTs is $C_{6Na_{4.152}}$ (1535 mAh·g$^{-1}$).

The changes to $E_b$ and $V_{OCV}$ as a function of Na concentration $x$ of $\gamma$GyNTs are shown in Figure 4c,f. For $(n, n)-\gamma$GyNTs, when $n = 2, 3,$ and $4$, respectively, the expected $C_{Na}^{max}$ were computed to be $C_{6Na_{2.36}}, C_{6Na_{1.83}},$ and $C_{6Na_{1.63}},$ with corresponding $E_b$ and $V_{OCV}$ values of $−1.11, −1.23,$ and $−1.23$ eV/Na and $0.04, 0.17,$ and $0.16$ V, respectively. For $(n, 0)-\gamma$GyNTs, when $n = 3, 4,$ and $5$, the $C_{Na}^{max}$ are expected to be $C_{6Na_{2.75}}, C_{6Na_{2.69}}, C_{6Na_{2.23}},$ respectively, and the $E_b$ and $V_{OCV}$ values are $−1.11, −1.14,$ and $−1.16$ eV/Na and $0.04, 0.07,$ and $0.10$ V, respectively. As shown in Figure 5c and Figure S7, as the structures approached $C_{Na}^{max}$, the distance of every Na to its nearest C atom was $2.65−2.74$ Å, indicating that every Na atom can strongly bind to the $\gamma$GyNTs via a chemical bond. Thus, the maximum storage Na capacity of $\gamma$GyNTs is $C_{6Na_{4.13}}$ (1535 mAh·g$^{-1}$).

Figure 6a shows the variations of maximum storage capacity as a function of tube size $(n)$ for all studied GyNTs. It is evident that, as $n$ increases, the $C_{Na}^{max}$ values monotonically decrease, except for those of $(3, 0)-\gamma$GyNT. Furthermore, the $C_{Na}^{max}$ of $(n, 0)$-GyNTs is greater than those of corresponding $(n, n)$-GyNTs with the same $n$, which is ascribed to the smaller radii of $(n, 0)$-GyNTs than $(n, n)$-GyNTs. The distinct behavior of $(3, 0)-\gamma$GyNT also originates from its smallest radius, which limits the storage of Na on the inner side. Therefore, we plotted the change of maximum storage capacity as a function of tube radius $(r)$ in Figure 6b. It is worth noting that the tube radius and the maximum capacity present an excellent correlation for all $\alpha, \beta,$ and $\gamma$GyNTs. The tube radius is an important determining factor of maximum capacity: a smaller tube radius leads to a larger area exposed by $\pi-\pi$ conjugation on the convex side of the GyNTs, which makes it more capable of adsorbing Na atoms. Furthermore, the $C_{Na}^{max}$ of $\alpha$GyNTs is always the largest, and that of $\gamma$GyNTs is always smallest for a given radius, which should originate from the difference in specific surface area. The specific surface areas of 2D $\alpha, \beta,$ and $\gamma$Gy are 21,089, 17,321, and 13,732 m$^2$/g, respectively.
Figure 6. The changes of maximum storage capacity as a function of (a) tube size and (b) tube radius.

3.3. Sodium Diffusion and Migration on GyNTs

For the GyNTs to be an excellent SIB anode, they must have not only a high specific capacity, but also a great rate performance. Herein, we calculated the diffusion path and migration energy barriers of Na on the convex and concave surfaces of (3, 0)-αGyNT, (2,0)-βGyNT, and (4, 0)-γGyNT, which exhibited the best Na storage ability of each GyNT type. For comparison, the Na diffusion on 2D Gy films was explored in advance. Figure S8a shows the calculated energy profile of Na diffusion along the favored path on αGy, and the energy barrier (ΔE‡) was computed to be 0.535 eV. Na diffusion on (3, 0)-αGyNTs will have more diffusion paths than that on αGy. We calculated the ΔE‡ of the favored diffusion path, H₀→H₁→H₂ for the convex surface and H₀'→H₁'→H₂' for the concave surface, as illustrated in Figure 7a,b. For the convex path, the ΔE‡ of H₀→H₁, H₁→H₂, and H₂→H₀ are, respectively, 0.818, 0.779, and 0.785 eV, which are slightly higher than that on αGy. On the concave path, the ΔE‡ values of H₀'→H₁', H₁'→H₂', and H₂'→H₀' significantly decrease to 0.047, 0.049, and 0.057 eV, respectively.

Figure S8b exhibits the Na diffusion on 2D βGy, for which the ΔE‡ of diffusion paths h₁→h₂, h₂→h₃, h₃→H, and H→h₁ are 0.549, 0.685, 0.662, and 0.0505 eV, respectively. The maximum ΔE‡ of Na on βGy is larger than that on αGy because βGy has a stronger adsorption capacity for Na. For Na on (2, 0)-βGyNTs, the simulated diffusion pathways are displayed in Figure 7c,d. The ΔE‡ values of h₁→h₂, h₂→h₃, h₃→H, and H→h₁ are 0.657, 0.727, 0.626, and 0.717 eV, respectively, whereas those of h₁′→h₂′, h₂′→h₃′, h₃′→H′, and H′→h₁′ are 0.089, 0.174, 0.093, and 0.100 eV. Figure S8c shows the Na diffusion on the 2D γGy, which has two diffusion paths, H₁→H₂ and H₂→H₁, with ΔE‡ values of 0.543 and 0.681 eV, respectively. For Na on (4, 0)-γGyNT, schematic drawings of the diffusion path and energy profiles are shown in Figure 7e,f. The ΔE‡ values on the convex and concave surfaces are 0.687, 0.591, 0.798, and 0.120 eV and 0.214, 0.352, 0.420, and 0.010 eV, respectively.

For all studied GyNTs, the ΔE‡ on the concave surface is much smaller than that on convex surface, which has to be attributed to the curvature effect that was discussed thoroughly in the previous study [41]. Thus, we conclude that GyNTs can provide good channels for diffusion of Na, and the ΔE‡ on αGy(NTs) and βGy(NTs) are smaller than that on γGy(NTs). Moreover, in addition to diffusion, the penetration of Na through GyNTs is another important factor for rate performance. For αGy(NTs) and βGy(NTs), the large size of the hexagonal acetylene rings promises easy penetration. In contrast, the pore sizes of γGy(NTs) are smaller than those of the other two types, which can inhibit penetration of Na. Figure S8d shows the Na penetrating γGy through H, whose ΔE‡ is up to 1.382 eV.
Relatively speaking, αGy(NTs) and βGy(NTs) should have better rate performance than γGy(NTs).

**Figure 7.** Schematics of the diffusion path and energy profiles for a sodium-ion on (a,b) (3, 0)-αGyNT, (c,d) (2, 0)-βGyNT, and (e,f) (4, 0)-γGyNT.

4. Conclusions

In summary, by carrying out density functional theory calculations, we investigated the applicability of α, β, and γ graphyne nanotubes (αGyNTs, βGyNTs, and γGyNTs, respectively) as SIB anodes. We predicted the maximum storage capacity of every studied graphyne nanotube by calculating the average binding energy and open-circuit voltage. The maximum storage capacity of every type of nanotube monotonically decreases with increases to the tube’s radius. The (3, 0)-αGyNT, (2, 0)-βGyNT, and (4, 0)-γGyNT had the maximum Na storage capacities of 1535, 1302, and 1001 mAh/g, respectively, for each type of GyNT. These values significantly exceed the largest reported values (N-doped graphene foams with 852.6 mAh/g capacity) in carbon materials. It was discovered that αGyNT has the largest, while γGyNT has the smallest storage capacity for a given tube size, which is ascribed to the fact that αGyNTs possess the larger specific surface area. The
NEB calculations reveal that Na ions can diffuse more easily into concave surfaces than on convex surfaces on a 2D film, which can promote migration of Na ions. Additionally, the large hexagonal acetylenic link can allow Na ions to easily penetrate, which can promote the diffusivity of Na ions. Overall, our results suggest that αGyNTs and βGyNTs are potential candidates as SIB anodes with ultra-high storage capacities and promising rate capabilities. Our study significantly enlarges the applicable field of graphyne materials.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12060670/s1, Figure S1: Optimized structure of all studied αGyNTs; Figure S2: Optimized structure of all studied βGyNTs; Figure S3: Optimized structure of all studied γGyNTs; Figure S4: Optimized structure of αGy (a), βGy (b), and γGy (c) when reaching the maximum storage Na capacities; Figure S5: Optimized geometries with maximum storage capacity of (a) (2, 2)-αGyNT, (b) (3, 3)-αGyNT, (c) (4, 4)-αGyNT, (d) (4, 0)-αGyNT, and (e) (5, 0)-αGyNT; Figure S6: Optimized geometries with maximum storage capacity of (a) (2, 2)-βGyNT, (b) (3, 3)-βGyNT, (c) (4, 4)-βGyNT, (d) (3, 0)-βGyNT, and (e) (4, 0)-βGyNT; Figure S7: Optimized geometries with maximum storage capacity of (a) (2, 2)-γGyNT, (b) (3, 3)-γGyNT, (c) (4, 4)-γGyNT, (d) (3, 0)-γGyNT, and (e) (5, 0)-γGyNT; Figure S8: Energy surfaces of Na diffusion on (a) αGy, (b) βGy, (c) γGy, and Na penetrates on (d) γGy.

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