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### Porous graphdiyne applied for sodium ion storage<sup>†</sup>

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Sodium ion batteries have gained recognition as an intriguing candidate for next generation battery systems and large scale energy storage devices due to the natural abundance of sodium sources. In this study, we prepared bulk graphdiyne powder with a porous structure and explored its sodium storage properties. The assembled sodium ion batteries exhibited extraordinary electrochemical performance, including moderate specific capacity, long cycle life as well as excellent rate performance, which should be attributed to its unique three-dimensional porous structure, chemical stability and high electronic conductivity. We obtained a reversible capacity of 261 mA h g<sup>-1</sup> after 300 cycles at a current density of 50 mA g<sup>-1</sup>. Even at a high current density of 100 mA g<sup>-1</sup>, the as-prepared GDY electrodes delivered a moderate specific capacity of 211 mA h g<sup>-1</sup> after 1000 cycles, with an excellent capacity retention of 98.2%. The calculation results indicate that most intercalated Na cations stay in a large triangular hole in bulk material.

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### Introduction

As human society is confronted with aggravating energy and environmental crises due to which great efforts have been devoted to the development of clean and renewable energy storage and conversion devices, including solar cells, fuel cells, water-splitting technology and rechargeable batteries.<sup>1</sup> Currently, lithium ion batteries (LIBs) are the most successful commercial rechargeable batteries and they are widely used in mobile devices and electric vehicles (EVs) due to their relatively higher energy density.<sup>2,3</sup> However, with the rapid growth of the need of large-scale applications, such as EVs and energy storage facilities, finding a substitute for Li to meet the growing demands for rechargeable batteries in large-scale applications is urgently needed because of the high cost and limited sources of Li. Recently, sodium (Na) ion batteries (SIBs) have been recognized as a promising alternative to LIBs for next generation battery systems and large-scale energy storage devices due to the natural abundance of sodium and the chemical similarities between Na and Li.4-6 However, it is difficult to find appropriate anode electrode materials as the ionic radius of Na<sup>+</sup> (102 pm) is larger compared to that of  $Li^+$  (76 pm), and the kinetics of Na<sup>+</sup> insertion and extraction are slower compared to that of Li<sup>+</sup>.<sup>5,7</sup> To correct this problem, a wide range of novel

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carbonaceous materials, such as hard carbon,<sup>8–10</sup> hollow carbon nanospheres<sup>11</sup> and nanowires,<sup>12</sup> carbon fibers,<sup>13,14</sup> graphite,<sup>15,16</sup> expanded graphite<sup>17</sup> and graphene,<sup>18–20</sup> have recently been investigated excessively and applied in SIBs, achieving a moderate capacity between 100 and 300 mA h g<sup>-1</sup>. These previous studies demonstrate the feasibility and potential of carbonaceous materials for next generation Na-based energy storage devices. However, these carbon-based anode electrodes in SIBs still suffer from low capacity and poor cycling stability, leading to the need for future efforts to improve their electrochemical performance continuously.<sup>21</sup>

The abovementioned results indicate that the morphology and pore size of carbon anodes play an important role in regulating the Na<sup>+</sup> transport and storage in SIBs. Recently, a novel carbon allotrope, graphdiyne (GDY), comprising sp- and sp<sup>2</sup>hybridized carbon atoms, has intrigued scientists deeply for its promising electronic, optical, and mechanical properties.<sup>22-30</sup> As a two dimensional (2D) layered carbon material consisting of delocalized  $\pi$  systems, GDY exhibits excellent chemical stability and high electrical conductivity<sup>25</sup> and is predicated to be the most stable compared with various diacetylenic non-natural carbon allotropes. The unique structure containing butadiyne linkages between the repeating hexatomic benzene main structure units could be the benefit of GDY with highly  $\pi$ -conjugated polymer structures, uniformly distributed pores, and tunable electronic properties, which supposedly enables it to show potential applications in photoelectrics, catalysis, gas separation, and energy storage fields.<sup>25,27,29-32</sup> Particularly, the density functional theory and the first-principles calculations have indicated that GDY is a promising anode material for both LIBs and SIBs with a maximum theoretical capacity of 744 mA h  $g^{-1}$ .<sup>32–35</sup> Therefore, we recently applied GDY films and bulk GDY powders as anode materials for LIBs and investigated their Li storage property.9,36

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The assembled LIBs exhibited superior electrochemical performance, including high specific capacity, excellent rate performance and long cycle life.

However, to the best of our knowledge, GDY has not been reported previously in the literature for its use in SIBs, except for the recent calculations reported by Lv et al.<sup>32</sup> To supplement the research in this field, we tried to explore the application of bulk GDY powder as an anode material for SIBs in this study (Fig. 1). GDY powder, with microporous and mesoporous structures, can be prepared easily according to the cross-coupling reaction, as reported previously.24,29 The assembled GDY-based SIBs anodes exhibit a reversible capacity of 261 mA h g<sup>-1</sup> achieved after 300 cycles at a current density of 50 mA  $g^{-1}$  and a high coulombic efficiency of >97% from the 10<sup>th</sup> cycle. Even at a higher current density of 100 mA  $g^{-1}$ , the as-prepared GDY electrodes deliver a moderate specific capacity of 211 mA h g<sup>-1</sup> after 1000 cycles and the capacity retention is as high as 98.2% from the 10<sup>th</sup> to the 1000<sup>th</sup> cycle. These results indicate that GDY is an efficient material for Na storage and has the potential to be applied in energy storage applications.

### Experimental

#### Methods

Copper powder was washed with 4 M HCl (100 mL), sonicated for 3 min, washed with water and EtOH, sonicated for 3 min, washed twice with acetone, and finally dried under N<sub>2</sub>. Washed copper powder and pyridine (50 mL) were charged in a threeneck flask; the mixture was heated at 120 °C under N<sub>2</sub> for 1 h and then the temperature was decreased to 80 °C. Hexakis [(trimethylsilyl)ethynyl]benzene (200 mg) was dissolved in THF (50 mL) in an ice bath (ice and NH<sub>4</sub>Cl) and purged with N<sub>2</sub> for 30 min. 1 M TBAF in THF (2.5 mL) was added under N<sub>2</sub> and then the mixture was stirred for 15 min at this low temperature (generally, the solution should be purple; this is related to the



Fig. 1 Schematic of a sodium ion battery based on GDY.

quality of the TBAF solution). The reaction mixture was diluted with EtOAc, washed three times with saturated NaCl, dried (MgSO<sub>4</sub>), and filtered. The solvent was evaporated under vacuum while maintaining the temperature below 30 °C (the deprotected compound should be rapidly processed in the dark and at low temperature to avoid decomposition). The residue was dissolved in pyridine (50 mL), transferred to a N<sub>2</sub>-protected constant addition funnel, and added dropwise into the mixture containing pyridine (50 mL) and copper powder at 80 °C (step 2); this addition process lasted for 8 h. The entire process, from deprotection to addition, should be continuous and rapid to avoid contact with oxygen. After addition of the deprotected compound, the reaction mixture was maintained at 120 °C for 3 days. Upon completion of the reaction, the pyridine was evaporated under reduced pressure. The crude products were washed sequentially with acetone and hot (80 °C) DMF. The combined crude product was washed with hot DMF to remove oligomers. The solid was heated sequentially under reflux at 100 °C for 8 h in 4 M NaOH, 6 M HCl, and 4 M NaOH to remove silicon and copper. The crude product was collected through centrifugation, washed sequentially with hot DMF (80 °C) and hot (70 °C) EtOH and then dried.

#### Materials characterization

Morphological information was obtained using field emission scanning electron microscopy (FESEM, HITACHI S-4800) and transmission electron microscopy (TEM, H-7650). Raman spectra were recorded at room temperature using a Thermo Scientific DXRxi system with excitation from an Ar laser at 532 nm. The X-ray photoelectron spectroscopy (XPS) results were collected on a VG Scientific ESCALab220i-XL X-ray photoelectron spectrometer using Al K $\alpha$  radiation as the excitation source. Nitrogen adsorption–desorption measurements were performed at 77 K using a Quantachrome Autosorb gas-sorption system.

#### **Electrochemical measurements**

The electrochemical experiments were performed in 2032 cointype cells. The electrodes were prepared by mixing 70 wt% GDY with 20 wt% Super P and 10 wt% polytetrafluoroethylene (PTFE) binders. The obtained GDY-based electrode samples were rolled into slices and cut into square pieces of 0.5 cm imes 0.5 cm (typically 2.0 mg cm<sup>-2</sup>) and then pasted on a stainless steel current-collector under a pressure of 15 MPa, followed by drying in a vacuum oven at 120 °C for 4 h, and used as the working electrode. Pure Na foil was used as the counter electrode, which was separated from the working electrode using a Celgard 2500 polymeric separator. The electrolyte was 1 M NaClO<sub>4</sub> in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1 : 1, v/v) containing 2% (by volume) fluoroethylene carbonate (FEC). The cells were assembled in an argon-filled glovebox with the concentration of moisture and oxygen less than 0.1 ppm. The galvanostatic charge-discharge cycling performance was measured using a LAND battery testing system in the voltage range from 5 mV to 3 V vs. Na/Na<sup>+</sup>. Cyclic voltammetry (CV) was performed using an

IM6 electrochemical workstation between 5 mV and 3 V  $\nu s.$  Na/Na $^{+}$  at a scan rate of 0.2 mV s $^{-1}.$ 

#### **Computational details**

All calculations were performed with the density functional theory (DFT) method using the GAUSSIAN 09 package.<sup>37</sup> The ground-state geometries of all species were optimized using the B3LYP functional<sup>38–40</sup> with the 6-31G(d) basis set. Dispersion correction was added to correctly take the intermolecular interactions into account. A rather simple approach was employed to provide an approximated understanding of the Na<sup>+</sup>-graphdiyne interactions. C<sub>30</sub>H<sub>12</sub> was taken to mimic the basic building block of graphdiyne. Various  $(Na<sup>+</sup>)_n-(C_{30}H_{12})$  geometries were constructed as initial guesses in the geometry optimization. The stabilities of the  $(Na<sup>+</sup>)_n-C_{30}H_{12}$  complexes were examined according to their formation energies, which refer to the relative energies of these species with respect to the energy summation of their individual species.

The following website is the official reference for the GAUSSIAN 09 citation: http://www.gaussian.com/g\_tech/g\_ur/m\_citation.htm

### **Results and discussion**

The structure of a GDY sheet is shown in Fig. S1a.† GDY contains butadiyne linkages between repeating carbon hexagon rings. The morphology of GDY powder was investigated via scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements. Fig. 2a shows that the GDY powder is composed of a 3D porous structure. The porosity of GDY was further characterized by nitrogen adsorption-desorption measurements, and the isotherm diagram is shown in Fig. 2b. Pore size distribution analysis clearly indicates that the pore-size is mainly at 1.41 and 2.77 nm. It is considered that the existing microporous and mesoporous structure of GDY is beneficial for the rapid transport of electrons and ions. Simultaneously, a high specific surface area of 287.7 m<sup>2</sup> g<sup>-1</sup> for GDY was obtained, as shown in Fig. 2b. As a result, the large surface area, together with the microporous and mesoporous structure, makes GDY favorable for fast diffusion of the relatively largesized sodium ions with a low ion-transport resistance and effective storage of Na ions during the discharge-charge processes.<sup>19</sup> The TEM image (Fig. 2c) further confirms this porous structure. The layer-to-layer distance of GDY was 0.365 nm, which was demonstrated by the HRTEM measurements (Fig. 1d). Fig. 2e and f illustrate the pore structure and interlayer spacing of multilayer GDY. Raman and X-ray photoelectron spectroscopy (XPS) measurements were carried out to further characterize the sample, and the results are in agreement with a previous report.<sup>30</sup> The detailed analysis will be shown in the ESI (Fig. S1<sup>†</sup>). The electronic conductivity was measured via UVvis absorption spectroscopy (Fig. S2<sup>†</sup>) and current-voltage (I-V) curve (Fig. S3<sup>†</sup>). The energy gap of GDY was measured to be 1.23 eV from the following relation:  $\alpha \propto (h\nu - E_g)^{1/2}/h\nu$ , which was obtained from the UV-vis absorption spectrum in Fig. S2.†  $h\nu$  is the photon energy, whereas  $\alpha$  is the optical absorption



Fig. 2 (a) SEM image of GDY. (b)  $N_2$  adsorption–desorption isotherms: the inset is the pore-size distribution of GDY. (c) TEM and (d) HRTEM images of GDY and (e and f) structural diagram of multilayer GDY.

coefficient, which is proportional to the absorbance (A).<sup>41</sup> This value of band gap is similar to that of silicon. Furthermore, the *I–V* curve, at a bias voltage of -10 V to 10 V, was also measured (Fig. S3†). It can be seen that the *I–V* curve of the porous GDY is approximately linear, which exhibits semiconductor behaviour, and the slope of the line was fitted to be  $4.4 \times 10^{-8}$ . The conductivity was calculated to be  $3.2 \times 10^{-4}$  S m<sup>-1</sup>, which was also similar to that of silicon, and this demonstrates that the porous GDY has a low carrier barrier that can be easily overcome under experimental conditions.

The electrochemical performance of GDY in terms of sodium storage was evaluated using 2032 coin-type half cells with a Na metal foil as the counter and reference electrode. It can be seen from Fig. 3a and b that the cyclic voltammogram (CV) curves and charge-discharge profiles are basically similar to the curves of GDY for Li storage,<sup>36</sup> only with a lower voltage and capacity. This is attributed to the difference between the thermodynamics and kinetics for the insertion of Li and Na ions because of the larger ionic radius of  $Na^+$  (102 pm) compared to that of  $Li^+$ (76 pm), which leads to a more sluggish insertion and extraction for Na<sup>+</sup>.<sup>21</sup> As shown in the CV profiles (Fig. 3a), an irreversible band appeared at about 0.75 V during the first cathodic scan, which was attributed to the formation of a solid electrolyte interface (SEI) film on the GDY-based electrode surface. A pair of asymmetric redox peaks could be observed in the low potential region of 0.005-0.3 V, with a larger cathodic branch than anodic branch, reflecting the voltage hysteresis phenomenon during the insertion/desertion reaction of Na<sup>+</sup> into and out of the GDY layers.42,43 Based on the differential voltage curves (Fig. 3b), the specific capacity in the region below 0.3 V could be attributed to the Na<sup>+</sup> intercalation into GDY layers, while the capacity above 0.3 V could be ascribed to the faradic capacitance on the surface or on the edge sites of GDY. Therefore, the Na<sup>+</sup> storage mechanism of GDY is a mixed process involving both Na<sup>+</sup> intercalating into GDY layers and absorbing onto the surfaces/interfaces or edges of GDY. This mixed storage mechanism is consistent with the previously reported mechanism of GDY for Li storage and of graphene for Li or Na storage.9,18,42,43 Fig. 3c displays the charge-discharge profiles of GDY-based electrodes, which were consistent with CV curves without distinguishing plateau and also similar with the curves



Fig. 3 (a) Cyclic voltammogram (CV) profiles of the GDY-based electrode at a scan rate of 0.2 mV s<sup>-1</sup>. (b) Differential curves of charge/ discharge profiles of the GDY-based electrode at a current density of 50 mA g<sup>-1</sup>. (c) Galvanostatic charge–discharge profiles at a current density of 50 mA g<sup>-1</sup> for the first three cycles. (d) Galvanostatic charge–discharge profiles at 50 mA g<sup>-1</sup> of the 10<sup>th</sup>, 50<sup>th</sup>, 100<sup>th</sup>, 200<sup>th</sup>, and 300<sup>th</sup> cycles.

of graphene for Na storage.<sup>18</sup> The bulk GDY powder exhibits a first cycle reversible specific capacity as high as 287.7 mA h g<sup>-1</sup> based on the total mass of electrode active materials, with the initial coulombic efficiency as low as 27.3% (ubiquitous in the abovementioned carbonaceous electrode materials, reported previously for sodium storage).

The rate capability of GDY powder was evaluated at different current densities ranging from 20 to 4000 mA  $g^{-1}$  (Fig. 4a). The reversible capacities at various charge–discharge rates were retained at 279, 257, 213, 176, 128, 84 and 56 mA h  $g^{-1}$  at current densities of 20, 50, 100, 200, 500, 1000 and 2000 mA  $g^{-1}$ , respectively. When the current density was reset to 20 mA  $g^{-1}$ , the capacity increased to 251 mA h  $g^{-1}$ , demonstrating the



Fig. 4 (a) Rate performance at varied current density ranging from 20 to 4000 mA  $g^{-1}$ . (b) Cycle performance at 50 mA  $g^{-1}$  and (c) cycle performance at a current density of 100 mA  $g^{-1}$ .

outstanding rate performance. Herein, the rate performance of Super P was also conducted in Fig. S4.<sup>†</sup> It can be observed that Super P exhibits a capacity of around 120 mA h g<sup>-1</sup> and the capacity contribution by Super P in our experiment was calculated to be approximately 34 mA h g<sup>-1</sup> at the current density of 50 mA g<sup>-1</sup>.

It can be seen from Fig. 4b that a reversible capacity of 261 mA h  $g^{-1}$  was achieved after 300 cycles at a current density of 50 mA  $g^{-1}$  and a high coulombic efficiency of >97% from the 10<sup>th</sup> cycle. The charge-discharge curves in Fig. 3d also clearly illustrate that the charge and discharge capacities at the 300<sup>th</sup> cycle are close to those at the 10<sup>th</sup> cycle, indicating outstanding cycle stability. Even at a high current density of 100 mA  $g^{-1}$ , the as-prepared GDY electrodes deliver a moderate specific capacity of 211 mA h  $g^{-1}$  after 1000 cycles, and the capacity retention is as high as 98.2% from the 10<sup>th</sup> to 1000<sup>th</sup> cycle (Fig. 4c). Even though the sodium storage capacity of GDY is similar to the reported hard carbon,<sup>8,10</sup> hollow carbon nanospheres<sup>11</sup> and nanowires,<sup>12</sup> expanded graphite<sup>17</sup> and reduced graphene oxide,<sup>18</sup> following a better capacity retention (Table S1<sup>†</sup>). The moderate specific capacity and long cycle life are attributed to the high specific surface area that endows GDY with abundant active sites for Na storage and excellent chemical stability of microporous and mesoporous GDY powders. The unique structure of GDY, with numerous micropores and mesopores, and the low barriers of Na ions diffusion are helpful for Na ions to rapidly transport on GDY, making the GDY suitable as a Na storage material, even at high charge-discharge rates. Moreover, a thick and stable SEI film takes a shape on the surface of porous GDY, which can be observed from SEM and TEM images after cycles in Fig. S5c and d.<sup>†</sup> The thickness of the SEI film is about 18 nm, as shown in Fig. S5e.† This uniform film is beneficial for a stable interface between bulk GDY materials and electrolyte. The superior electrochemical performance, in terms of Na storage, benefits from the high electronic conductivity, excellent chemical stability of GDY, and fast diffusion of Na ions in its microporous and mesoporous structure. All these results indicate that GDY is a promising anode material for SIBs with high capacity, outstanding rate capability and long cycle life.

To explain the excellent performance of GDY as an anode material for SIBs, density functional theory (DFT) was used to investigate the sodium storage in GDY. Ly figured out that the distance of two layers needed to become significantly longer, from 3.5 to 4.2 Å, in order to capture three Na<sup>+</sup>.<sup>32</sup> In our experiments, the well-stacked GDY maintained a stable cycle performance, which implies that the layer distance of GDY is hard to change due to the high van der Waals interactions. Hence, in our calculations, we focused on the case without large geometry deformation of the GDY interlayer structure with layer distance of around 3.65 Å. Herein, we focused on the qualitative understanding of the interaction between Na cations and the building unit of GDY, which was mimicked by C<sub>30</sub>H<sub>12</sub>. The stabilities of  $(Na^+)_n$ -C<sub>30</sub>H<sub>12</sub> complexes were examined according to their formation energies, which refer to the relative energies of these species with respect to the energy summation of individual species. When only one Na cation was added, two possible Na<sup>+</sup>-C<sub>30</sub>H<sub>12</sub> configurations were obtained, whose

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energies are lower than the energy summation of Na<sup>+</sup> and  $C_{30}H_{12}$  (Fig. 5). The Na cation may be located either in the center of the large triangular hole (Fig. 5, A1) or above the benzene ring plane (Fig. 5, A2). Both configurations show similar stability with a small energy difference of  $\sim 0.12$  eV. When two Na cations were added, several stable geometries B1-B4 (Fig. 6) could be obtained. At the most stable B1 configuration, with largest negative formation energy, one Na cation was located in the center of the big triangle hole and the other Na<sup>+</sup> appeared above the benzene ring. Two less stable B2 and B3 configurations show numerous similarities, both in geometries and energies, while they differ by the fact that the two Na cations may stay in either the same or different sides of the ring plane. It is also possible that both Na cations are located in the center of the big triangle hole. However, this complex pattern does not look very feasible due to the significant distortion of the triangular framework. When three Na<sup>+</sup> ions were taken into account, all optimized complexes were unstable because their energies were higher than the energy summation of the three Na cations and one  $C_{30}H_{12}$  (see Fig. 7). Overall, the stability of the complex dramatically decreased when more Na cations were introduced.

Thus, if the maximum number of Na cations exists in the Na<sup>+</sup>–GDY complex, only a limited number of configurations may be possible (Fig. 8). In the A1 configuration, all Na cations may exist in the large triangular hole of GDY. In the A2 configuration, all Na cations may stay on top of the benzene ring. Since the size of the Na cation is not very small and the distance of two stacked GDY layers is around 3.65 angstrom, the A1 configuration in Fig. 8 should be more preferred in principle.



Fig. 5 The geometries and formation energies of two optimized  $Na^+ - C_{30}H_{12}$  complexes (A1 and A2).



Fig. 7 When 3 Na<sup>+</sup> ions were taken into account, all optimized (Na<sup>+</sup>)\_n-C\_{30}H\_{12} complexes were unstable.

Although the A2 and B1 configurations in Fig. 8 may not be preferred in well-stacked GDY layers due to limited interlayer space, they may still be possible in realistic GDY materials because several local domains should display imperfectly stacked or unstacked layers.

Theoretically, the stable A1 configuration (Fig. 8) corresponds to a storage capacity of 248 mA h  $g^{-1}$  (NaC<sub>9</sub>). As for the A2 and B1 configurations (Fig. 8), although it is unstable for Na<sup>+</sup> staying on top of the benzene ring between two well-stacked graphdiyne layers, the structure may exist on the surface or non-well stacked graphdiyne layer of the GDY (124 mA h  $g^{-1}$ , NaC<sub>18</sub>). As the specific surface area was 287.7 m<sup>2</sup> g<sup>-1</sup>, as demonstrated by nitrogen adsorption–desorption measurements, and the theoretical mass density of monolayer GDY was 0.46 mg m<sup>-2</sup>,<sup>9</sup> the Na<sup>+</sup> staying on top of the benzene ring on the surface of GDY could contribute a storage capacity of 16.4 mA h g<sup>-1</sup>. With the A1 configuration for the bulk and B1 for the surface of GDY, the theoretical intercalation storage capacity of GDY should be 264.4 mA h g<sup>-1</sup>.

In a realistic GDY, surface and edge of atoms exist and are different from the bulk atoms. Hence, abundant Na<sup>+</sup> ions were always adsorbed on these atoms and resulted in faradic capacitance. As for the maximum adsorbed sodium storage concentration on the surface of GDY, the NaC<sub>3</sub> (744 mA h g<sup>-1</sup>) would be preferred, which was reported by Lv *et al.*<sup>32</sup> Moreover, the C–H on the edge of GDY also plays an important role in SIBs, as reported by Goodenough's group.<sup>44</sup> These results indicate that most intercalation Na cations stay in the large triangular



Fig. 6 Four possible geometries B1–B4 of  $(Na^+)_2$ –C<sub>30</sub>H<sub>12</sub>.



Fig. 8 Possible configurations of the Na<sup>+</sup>-GDY complexes.

hole and a large amount of Na cations adsorb onto the surface and edges of GDY.

### Conclusion

In conclusion, GDY powders with porous structure were successfully synthesized and applied as electrode materials for Na storage. The assembled GDY-based SIBs exhibited excellent electrochemical performance, including moderate reversible specific capacity, long cycle life and outstanding rate performance. The Na storage mechanism of GDY is a mixed process involving both Na<sup>+</sup> intercalating into GDY layers and absorbing onto the surfaces/interfaces or on the edges of GDY. The unique structure of GDY, with numerous micropores and mesopores, endows GDY with more Na storage sites and facilitates the rapid transport of electrons and ions. We believe that designing and preparing novel carbon-based materials with porous structures might open up an approach to develop new electrode materials with high capacity and excellent cycling stability for satisfying the future requirements of Na-ion-based energy storage devices.

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