



Article Continuously Interconnected N-Doped Porous Carbon for High-Performance Lithium-Ion Capacitors

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Abstract: Lithium-ion hybrid capacitors (LICs) possess the fascinating characteristics of both high power density and high energy density simultaneously. However, to design highly compatible cathode materials with a high capacity and anode materials with a high rate performance is still a major challenge because of the mismatch of dynamic mechanisms, greatly limiting the development of LICs. Herein, we report an N-doped porous carbon (N-PC) with a continuously interconnected network as the cathode, matching the dynamic mechanism of the uniquely pseudocapacitive T-Nb₂O₅ anode without diffusion-controlled behavior. This heteroatom-grafting strategy of the cathode can effectively control the dynamic process to adjust the ion transport efficiency, shortening the gap of kinetics and capacity with the anode. For the energy storage application, the as-prepared N–PC cathode demonstrates an appreciable capacity of 62.06 mAh g^{-1} under a high voltage window of 3 V to 4.2 V, which can exceed the capacity of 25.57 mAh g^{-1} for porous carbon without heteroatom doping at the current density of 0.1 A g^{-1} . Furthermore, the as-developed lithium-ion capacitor possesses an outstanding electrochemical performance (80.57 Wh kg⁻¹ at 135 W kg⁻¹ and 36.77 Wh kg⁻¹ at 2.7 kW kg⁻¹). This work can provide a new avenue to design cathode materials with a highly appreciable capacity and highly compatible kinetic mechanism, further developing high-performance lithium-ion capacitors.

Keywords: lithium-ion hybrid capacitors; N-doped porous carbon; interconnected network; electrochemical performance

1. Introduction

With the rapid development of urban rail transit, aerospace, and smart grids, electrochemical energy storage devices with the advantages of greenness, efficiency, and sustainability can effectively realize the storage of electric energy, providing a stable energy output [1–4]. Among them, lithium-ion capacitors (LICs), combining the outstanding power characteristics of supercapacitors and the attractive energy characteristics of batteries, have attracted extensive attention from researchers [5–8]. Nevertheless, the dynamic mismatch problem, originating from the surface energy storage mechanism between physical adsorption and faradaic process, tremendously limits the development of hybrid capacitors [9–12]. Consequently, it is extremely vital for high-performance hybrid capacitor production that we design highly compatible cathode materials matching the anode materials with similar kinetics and capacity [13].

Commercial activated carbon (AC) with a large surface area, cycling stability, stable chemical properties, and excellent electrical conductivity has attracted the attention of researchers as a cathode material [14–19]. Unfortunately, electrolyte ions with a large diameter may find it difficult to enter the interior micropores of this commercial AC, severely limiting the rapid transmission and effective storage of ions [20]. Changing the electron distribution and realizing surface functionalization is an effective method to change



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). carbon atoms, can easily enter the lattice structure of carbon and benefit the doping of the nitrogen atom [26–29]. From the perspective of a preparation strategy, nitrogen-doping treatment on the as-prepared porous carbon can retain the morphology and pore structure of the original carbon material at high temperatures, but the increase in graphitization degree may not increase the existence of heteroatoms [30,31]. From the perspective of carbon network construction, carbon materials prepared by chemical activation show abundant defects and a discontinuous internal network, further hindering the rapid transmission of charge [32,33]. Typically, Nb₂O₅ possesses the prominent superiority of a high theoretical capacity (200 mAh g^{-1}) and a relatively low working voltage (1.0~1.5 V vs. Li⁺/Li), providing the two-dimensional transport channels for ions [34]. Interestingly, an Nb_2O_5 crystal without diffusion-controlled behavior intrinsically possesses the typical intercalation pseudocapacitance in the bulk phase, making it a promising anode of LICs. However, it is difficult to find a well dynamic-matched cathode with this unique Nb_2O_5 anode. In this regard, the design of highly compatible cathode materials is a feasible strategy to match the dynamic behavior of Nb_2O_5 . Thus far, the field still lacks a controllable and efficient strategy to control the dynamic process at an atom scale to adjust the ion transport efficiency, shortening the gap of kinetics and capacity with the anode.

Here, we construct an N-doped porous carbon (N-PC) with a continuously interconnected network via a heteroatom-grafting strategy at an atom scale, matching the dynamic process of T-Nb₂O₅ with a hierarchically spherical structure as the anode. N-doped porous carbon, conducting the formation of a porous structure and the doping of nitrogen simultaneously, can exhibit rich nitrogen atoms (3.95%) and abundant defects. In our strategy, different nitrogen configurations, consisting of pyridinic nitrogen, pyrrolic nitrogen, and graphitic nitrogen, can effectively graft the discontinuous carbon network based on KOH molecule activation during a high-temperature reaction, further adjusting the electron distribution and improving the utilization of the effective specific surface area (SSA) in the carbon structure. Therefore, the suitably hierarchical pore structures possess a notable SSA $(2419 \text{ m}^2 \text{ g}^{-1})$ and an efficient electrochemically active surface, further showing their excellent power characteristics. Based on it, the as-developed lithium-ion capacitor can deliver a high energy density of 80.57 Wh kg $^{-1}$, showing excellent electrochemical characteristics. Furthermore, the heteroatom-grafting strategy will provide a new avenue to design continuously interconnected carbon networks with a high proportion of heteroatoms.

2. Results and Discussion

Our strategy involving using KOH molecules and melamine molecules controllably builds N–PC with a continuously interconnected network. As shown in Figure 1a, nitrogen atoms based on different bonding mechanisms can realize the grafting of discontinuous carbon networks. Without the addition of melamine, the internally and externally doubleactivated KOH molecules could consume a large number of carbon atoms for producing a large number of micropores (Figure S1). Large-size electrolyte ions, such as PF_6^- , can have difficulty achieving rapid transmission and effective storage in micropores. Therefore, the introduction of melamine molecules can be conducive to improving the continuity of the carbon network as the cathode, and the melt-etching mechanism can effectively regulate the pore structure. As an anode material, $T-Nb_2O_5$ possesses a hierarchically spherical structure, open skeleton, and excellent chemical stability. As shown in Figure 1c, $T-Nb_2O_5$ can reversibly embed and exfoliate Li⁺ while avoiding a significant volume expansion effect, and its inherent pseudocapacitance can accelerate the reaction kinetics, making up for the problem of the poor rate performance caused by intrinsic conductivity. After understanding the energy storage mechanism of N-PC and $T-Nb_2O_5$, active materials could be used as the electrode of the lithium-ion capacitor through balancing the dynamic mechanism (Figure 1b). Capacitive-type cathodes adsorbed by PF_6^- ions in electrolyte can



form an electric double layer to store energy during the charging process, and the Li⁺ ions can be embedded in the battery-type anode.

Figure 1. Schematic diagram of the charge storage mechanism for the high-performance lithium-ion capacitor. (**a**) Bonding mechanisms of nitrogen atoms for grafting the carbon networks. (**b**) Schematic diagram of charge transportation. (**c**) Schematic diagram of $T-Nb_2O_5$ with a hierarchically spherical structure for anode materials. (**d**) Typical TEM image of N-PC showing the lamellar structure with abundant defects. (**e**) Deconvolution curves of the N1s of N-PC. (**f**) XRD patterns of T-Nb₂O₅. (**g**) Typical TEM image of $T-Nb_2O_5$ showing the obvious lattice array.

Figure 1d and Figure S2 present the lamellar structure with abundant defects through the mechanism of high-temperature melting, evidently proving that the introduction of nitrogen atoms can be helpful to adjust the continuity of carbon. As shown in Figure 1e and Figure S3, XPS measurement was used to determine the element composition, element contents, and element configuration of N–PC. In the N 1s spectra, four obviously fitted peaks appear at 398.7, 399.6, 400.6, and 402.0 eV, corresponding to pyridinic N, pyrrolic N, graphitic N, and oxidized pyridinic N, respectively. Notably, the fitted N-6 and N-5 can produce partial pseudocapacitance, and graphite nitrogen can improve the conductivity of N-PC (Table S1) [35]. According to the XRD analysis (Figure 1f), the large spacing of the (001) peak can accommodate a large amount of Li⁺, and the (180) peak can provide a natural transmission channel, benefiting the rapid occupation of Li⁺ in many empty octahedral sites between the crystal plane of the (001) peak [36]. TEM measurement also proves that T–Nb₂O₅ possesses an obvious lattice array (Figure 1g and Figure S4).

Figure 2a vividly illustrates the formation mechanism of N–PC with a continuously interconnected network. Firstly, melamine may have difficulty entering the interior of the ramie precursor embedded by KOH molecules through mechanical mixing at room temperature. Subsequently, melamine molecules with the function of melt etching can be transformed into a carbon nitride allotrope (g-C₃N₄) by the process of high-temperature activation, and enter into the interior of self-defective ramie carbon simultaneously, filling the corresponding defects caused by chemical activation [37,38]. Eventually, the g-C₃N₄ decomposes to form some nitrogen-containing groups (C₂N₂⁺, C₃N₃⁺, and C₃N₂⁺), playing the role of atomic regulation [39]. As shown in Figure 2b and Figure S5, N–PC possesses a three-dimensionally interconnected skeleton structure and rough surface with abundant

microstructures, indicating the melt-etching reaction between nitrogen-containing groups and carbon atoms in the process of high-temperature carbonization. TEM images can be further used to characterize the morphology and structure of the as-prepared N-PC, revealing that nitrogen atoms can effectively adjust the lamellar microstructure to achieve the goal of improving the chemical activity of porous carbon (Figure 2c). As shown in Figure 2d, carbon nanosheets exhibit abundantly disordered and evenly distributed porous structures, providing sufficient adsorption sites for electrolyte ions to improve the electrochemical properties. EDS spectra can be used to confirm the complete removal of impurity elements and the uniform doping of N atoms (Figure 2e). To further determine the element composition, element contents, and element configuration of N–PC, XPS measurements showed three apparent peaks at 284.0, 400.1, and 533 eV, corresponding to C 1s, N 1s, and O 1s (Figure 2f, Tables S2 and S3). As shown in Figure 2g and Figure S6, Raman spectroscopy can be used to determine the defect and disorder degree of the N–PC. By calculating the area of the D-peak and G-peak, the I_D/I_G values of PC and N–PC are 3 and 3.44, respectively. The introduction of heteroatoms can be conductive to improving the disorder and defect degree of the structure, and increasing the adsorption sites of electrolyte ions, improving the capacitance performance [40].



Figure 2. Structural design of N-doped porous carbon (N-PC). (a) Heteroatom-grafting strategy for the synthesis of N-PC with a continuously interconnected network. (b) Respective SEM image of N-PC with a three-dimensional skeleton structure and rough surface. (c) Typical TEM image of N-PC with a lamellar microstructure. (d) TEM image of N-PC with abundantly disordered structures. (e) Element mapping images of N-PC for N, C, O, and K elements. (f) XPS survey of N-PC. (g) Raman spectrum of N-PC.

As shown in Figure 3a and Figure S7, $T-Nb_2O_5$ is composed of nanoparticles. Among them, citric acid plays the role of surfactant in the reaction process, benefiting the formation of a spherical morphology. With an increase in calcination temperature, the micro-morphology of Nb₂O₅ can change from spherical to rectangular (Figure 3b and Figure S4). Figure 3c displays the maximum crystal plane spacing of 0.39 nm determined through high-resolution TEM images, and the selected area diffraction (SAD) reveals the lattice array of the $T-Nb_2O_5$ in the illustration, corresponding to (001), (180), and (181) respectively. Element distribution diagrams of the $T-Nb_2O_5$ vividly reveal the uniform distribution of the Nb element and O element (Figure 3d). As shown in Figure 3e, XPS measurements can be used to determine the chemical valence of the as-prepared $T-Nb_2O_5$. Remarkably, the Nb element and O element of $T-Nb_2O_5$ occupy a large proportion, indicating their high purity after annealing. The two characteristic peaks with binding energies at 207.7 and 210.5 eV reveal Nb $3d_{5/2}$ and Nb $3d_{3/2}$ peaks respectively, corresponding to the +5 valence of Nb (Figure 3f) [41]. In the O 1s spectra, two obviously fitted peaks appear at 529.12 and 530.6 eV, proving the presence of the Nb–O bond and hydroxylated surface (Figure 3g). As shown in Figure 3h, $T-Nb_2O_5$ exhibits a relatively low adsorption platform. Obviously, the isotherm encounters difficulty forming a platform with a relative pressure of $P/P_0 = 1$, indicating that the adsorption fails to reach saturation. The pore size distribution of $T-Nb_2O_5$ mainly presents a large number of mesopores, corresponding to an average size of 6.74 nm. Interestingly, the above $T-Nb_2O_5$ shows a relatively low SSA (30.35 m² g⁻¹), which can be conductive to the rapid intercalation of ions for maintaining a high coulomb efficiency. Regarding T-Nb₂O₅ in crystal form, nanostructure and SSA can affect the behavior of embedded pseudocapacitance (Figure 3i).



Figure 3. Morphology and physical analysis of $T-Nb_2O_5$. (a) Respective SEM image of $T-Nb_2O_5$ with abundant nanoparticles. (b) Typical TEM image of Nb_2O_5 with a spherical micro-morphology. (c) High-resolution TEM images reflecting the maximum crystal plane spacing. (d) Element mapping images of $T-Nb_2O_5$ for Nb, O, C, and Cl elements. (e) XPS survey of $T-Nb_2O_5$. (f) Deconvolution curves of the Nb3d of $T-Nb_2O_5$. (g) Deconvolution curves of the O1s of $T-Nb_2O_5$. (h) Pore size distribution of $T-Nb_2O_5$. (i) Schematic diagram of $T-Nb_2O_5$.

After understanding the structural properties of N-PC with a continuously interconnected network and $T-Nb_2O_5$ with hierarchically spherical structure, the N-PC based electrode and T-Nb2O5 based electrode can be used to assemble half cells for electrochemical testing (Figure 4a). According to the nitrogen adsorption isotherm, the N_2 adsorption quantity of N–PC increases sharply at the relative pressure of $P/P_0 < 0.05$, indicating a large number of microporous structures, while the N_2 adsorption quantity of N-PCimproves continuously at the relative pressure of $0.05 < P/P_0 < 0.9$, proving the abundant mesoporous structure (Figure S8). As shown in Figure 4b and Table S4, N-PC possesses a prominent SSA (2419 m² g⁻¹) and a high pore volume (1.09 cm³ g⁻¹). Among them, the pore volume of the mesoporous structure is about 0.63 cm³ g⁻¹, benefiting the regulation of the hierarchical pore structure through the melt etching of melamine. EIS spectra can reflect the charge transfer resistance of N-PC (Figure 4c). Theoretically, the smaller semicircle can be conductive to electron transmission behavior in the high frequency region, proving that the high content of nitrogen atoms can effectively enhance the electronic conductivity of N–PC. As shown in Figure 4d and Figure S9, the CV curve represents a regularly rectangular shape. With an increase in scan rate, the N-PC-based electrode still has no polarization deformation, illustrating the improvement of both electron and ion transmission capacity. Figure 4e and Figure S10 present the charge and discharge curve of N-PC under a higher voltage window of 3 V to 4.2 V, corresponding to the capacity of 62.06 mAh g^{-1} . Even if the current density is increased to 5 A g^{-1} , the as-prepared N–PC demonstrates a capacity of 23.81 mAh g^{-1} , showing an excellent rate performance.



Figure 4. Electrochemical properties of the N–PC cathode. (a) Schematic diagram of charge transportation for the N–PC cathode. (b) Pore size distribution of N–PC and PC. (c) Nyquist plots. (d) CV curves at a scan rate of 10 mV s⁻¹. (e) GCD curves at a current density of 0.1 A g⁻¹.

Furthermore, the redox potential of $T-Nb_2O_5$ can effectively avoid the formation of lithium dendrites and piercing the diaphragm to cause an internal short circuit, resulting in safety problems (Figure S11). As shown in Figure 5a, $T-Nb_2O_5$ can exhibit a capacity of 194.39 mAh g⁻¹ at 0.1 A g⁻¹ under the voltage window of 1 V to 3 V. Obviously, potential platform difficulties can be discovered, reflecting the pseudocapacitance behavior of the reactive process. The CV curve evidently presents redox peaks, corresponding to an electrochemical reaction in the process of Li⁺ embedding and stripping (Figure 5b). Remarkably, the capacity of $T-Nb_2O_5$ -based electrode increases from 58.16 mAh g⁻¹ to 185.58 mAh g⁻¹ through directly adjusting the current density from 5 A g⁻¹ to 0.1 A g⁻¹, further illustrating the strong stability and reversibility of $T-Nb_2O_5$ (Figure 5c). As shown in Figure 5d, the intrinsic capacity of capacitive charge is about 55 mAh g⁻¹ through the

intercept of the fitting line on the y-axis. By further analyzing the CV curve, the ratio of capacity contribution can be determined in the process of capacitance and diffusion control (Figure 5e). Therefore, the total charge storage can be expressed as the sum of the capacitive charge storage and diffusion-controlled charge storage. The formula is as follows [42]:

$$i(V) = k_1 v + k_2 v^{1/2} \tag{1}$$

where the values of k_1 and k_2 can determine the proportion of current contributions at a specific voltage. According to the quantitative analysis, the pseudocapacitance contribution of the electrode accounts for 11.16% of the total charge storage (Figure 5f). The outstanding performance of nanostructured T–Nb₂O₅ can be attributed to the following points: (a) Li⁺ can be embedded along a favorable path of crystal structure; (b) interconnected crystal planes can form open channels, resulting in a reduction in energy barriers.



Figure 5. Electrochemical properties of the $T-Nb_2O_5$ anode. (a) GCD curves at different current densities. (b) CV curves at different scan rates. (c) Rate performance of the $T-Nb_2O_5$ anode. (d) Voltammetric capacity. (e) CV curve at a scan rate of 5 mV s⁻¹. (f) Contribution of diffusion-controlled charge storage and capacitive charge storage.

A high-performance lithium-ion capacitor was fabricated using N-doped porous carbon (N–PC) with a continuously interconnected network as the cathode and $T-Nb_2O_5$ with a hierarchically spherical structure as the anode. Importantly, the proportional relationship between the positive and negative active substances is the key to realizing high-performance lithium-ion capacitors. As shown in Figure 6a, the capacity of N–PC is about 62.06 mAh g⁻¹ under the voltage window of 3-4.2 V, while the capacity of $T-Nb_2O_5$ is about 181 mAh g^{-1} in the voltage window of 1-2.5 V under the same current density. Therefore, the mass ratio of active substances can be determined to be 1:2.9 based on the capacitive matching principle of anode and cathode. The lithium-ion capacitor shows a shape similar to a rectangle from the CV curves, indicating an excellent capacitance behavior (Figure 6b). The GCD curve exhibits symmetrical triangles, proving an excellent synergistic effect of the different charge storage mechanisms, exhibiting outstanding capacitance characteristics (Figure 6c). As shown in Figure 6d, the capacity of the lithium-ion capacitor increases from 25.07 mAh g^{-1} to 44.4 mAh g^{-1} through directly adjusting the current density from 2 A g^{-1} to 0.1 A g^{-1} , presenting a high capacity retention of 96.52% to illustrate the strong stability and reversibility of such devices. The electrochemical



reaction can be analyzed by the relationship between the scan rate and response current, the relationship is as follows:

$$i(v) = av^b \tag{2}$$

$$\log i(v) = \log a + b \log v \tag{3}$$

Figure 6. Electrochemical properties of the high-performance lithium-ion capacitor. (a) Capacity at different current densities for the N–PC cathode and T–Nb₂O₅ anode. (b) CV curves at different scan rates. (c) GCD curves at different current densities. (d) Rate performance of the lithium-ion capacitor. (e) Calculation curve of b-values at different scan rates of $1-10 \text{ mV s}^{-1}$. (f) Ragone plots of the high-performance lithium-ion capacitor and others reported in the literature. (g) Cycling stability of the lithium-ion capacitor.

Figure 6e reveals the calculation curve of the *b*-values at redox potential at different scan rates, corresponding to *b*-values of 0.859 and 0.747, respectively, during charging and discharging, indicating that dynamic behavior can be mainly controlled by capacitance to exhibit excellent kinetic behavior in the process of charging. As shown in Figure 6f, the as-developed lithium-ion capacitor can output an energy density of 80.57 Wh kg⁻¹ at 135 W kg⁻¹, while the power density can be increased to 2700 W kg⁻¹, corresponding to an energy density of 36.77 Wh kg⁻¹ [43–49]. Cycle performance and coulombic efficiency can be used to analyze the cycle stability of the lithium-ion capacitor. Remarkably, the device possesses a capacity retention rate of 89.43% after 10,000 cycles, proving an outstanding cycle performance (Figure 6g).

Cathode active materials with a low capacity have a higher proportion of active substances, limiting the improvement of the energy density of lithium-ion hybrid capacitors. The outstanding performance of the as-prepared lithium-ion capacitor can be attributed

to the compatibility of kinetics and capacity between the cathode and anode. Importantly, N-doped porous carbon (N–PC) possesses a continuously interconnected network and abundant active sites, improving the matching of the dynamic mechanisms. First, N–PC was synthesized using melt-etched melamine molecules and self-defective ramie carbon simultaneously. Second, a carbon nitride allotrope (g-C₃N₄) could enter into the interior of the self-defective ramie carbon, filling the corresponding defects caused by chemical activation. Furthermore, nitrogen atoms, entering the lattice of carbon atoms, can deform the lattice, effectively increasing the active sites and electron density. Therefore, the N–PC with increased ion adsorption sites, ion transfer rates, and electrochemical cycle stability can remarkably improve on pure carbon materials. More importantly, the heteroatom-grafting strategy can successfully design continuously interconnected carbon networks, promoting their applications in catalysis and semiconductors.

3. Conclusions

In summary, we reported a heteroatom-grafting strategy to effectively build an interconnected network by using the bonding mechanism of nitrogen atoms, solving the compatibility of kinetics and capacity between cathode and anode. In the heteroatom-grafting strategy, a carbon nitride allotrope $(g-C_3N_4)$ could enter the interior of self-defective ramie carbon, filling the corresponding defects to realize the continuity of the carbon network. By adjusting the structure and surface chemical state of carbon materials, the introduction of heteroatoms significantly improved the capacity of the cathode. Remarkably, N–PC possessed an outstanding SSA of 2419 m² g⁻¹ and a high pore volume of 1.09 cm³ g⁻¹, benefiting the regulation of the hierarchical pore structure through the melt etching of melamine. Based on these results, a high-performance lithium-ion capacitor could be fabricated using the N-doped porous carbon (N-PC) with a continuously interconnected network as the cathode and T-Nb₂O₅ without diffusion-controlled behavior as the anode. For energy storage applications, the as-developed lithium-ion capacitor delivered a high energy density of 80.57 Wh kg⁻¹ at 135 W kg⁻¹ and high power density of 2700 W kg⁻¹ at 36.77 Wh kg⁻¹, showing an outstanding electrochemical performance. This study can be unambiguously helpful in understanding the structure-activity relationship between material properties, structure, and surface state, providing the design method to build electrode materials with an outstanding performance, and promoting the development of high-performance hybrid capacitors.

4. Experimental Section

Chemicals reagent and quantity: Ramie originated from Dazhu, Chengdu, China. Potassium hydroxide, melamine, hydrochloric acid, citric acid, niobium chloride, and anhydrous ethanol were acquired from Chengdu Kelong Chemicals Co., Ltd., China.

Preparation of T-Nb₂O₅ with hierarchically spherical structure: Nb₂O₅ nanoparticles with different phase structures were synthesized by a simple hydrothermal treatment and high-temperature treatment. Firstly, 0.27 g niobium chloride (NbCl₅) was dissolved in 5 mL anhydrous ethanol and stirred continuously in an ice bath for 1 h, obtaining the niobium ethoxide solution. Then, the solution was prepared by adequately mixing the niobium ethoxide solution, an aqueous solution of hydrochloric acid (5 mL deionized water was used to dissolve 1.5 g HCl), and an aqueous solution of citric acid (15 mL deionized water was used to dissolve 2.25 g citric acid monohydrate). Sequentially, the precursors, heated at 200 °C for 24 h in the stainless-steel autoclave, were obtained through hydrothermal treatment, and naturally cooled to room temperature after the reaction. Nb₂O₅ precursors were cleaned using anhydrous ethanol and deionized water, and dried at 70 °C. Finally, the as-prepared nanoparticles with different phase structures were synthesized through heating to selected temperatures (600 °C, 700 °C, and 800 °C) for 6 h under an Ar₂ atmosphere.

Preparation of porous carbon (PC): Porous carbon was synthesized by a self-defective strategy of ramie-embedded KOH molecules. Firstly, 1 g nature ramie was distributed in 30 mL of 3 M KOH solution under a Teflon-lined reactor. Then, the reactor was heated to

180 °C for 6 h in an oven, obtaining the ramie precursors embedded with KOH molecules. After naturally cooling to room temperature, the ramie precursors obtained by suction filtration were placed in an oven with a selected temperature of 70 °C for 12 h. Sequentially, both 0.9 g ramie precursors and 0.45 g KOH powder were evenly mixed, and the mixture was transferred to the tube furnace. Importantly, the mixture was reacted for 1 h at the target temperature of 700 °C under an Ar₂ atmosphere. After the tubular furnace cooled to room temperature, the impurities of the sample were removed using 1 M HCl solution for 8 h, and a large amount of deionized water was used to dislodge the excess acid molecules. Finally, the as-prepared porous carbon (PC) was dried at 110 °C for 12 h.

Preparation of N-doped porous carbon (N–PC): N-doped porous carbon was synthesized by a grafting strategy of nitrogen configurations based on melt etching. Firstly, 1 g nature ramie was distributed in 30 mL of 3 M KOH solution under a Teflon-lined reactor. Then, reactor was heated to 180 °C for 6 h in an oven, further obtaining the ramie precursors with embedded KOH molecules. After naturally cooling to room temperature, the ramie precursors obtained by suction filtration were placed in an oven with a selected temperature of 70 °C for 12 h. Sequentially, 0.9 g ramie precursors, 0.45 g KOH powder, and different quality of melamine powder (0.1 g, 0.15 g, 0.2 g, and 0.25 g) were evenly mixed, and the mixture was transferred to the tube furnace. Importantly, the mixture was reacted for 1 h at the target temperature of 700 °C under an Ar₂ atmosphere.

After the tubular furnace cooled to room temperature, the impurities of the sample were removed using 1 M HCl solution for 8 h, and a large amount of deionized water was used to dislodge the excess acid molecules. Finally, the as-prepared N-doped porous carbon (N-PC) was dried at 110 °C for 12 h.

5. Characterization Methods

SEM (JEOL JSM–7800 Prime) and TEM (JEOL JEM-2100F) were used to observe the surface morphology and size of the as-prepared active materials. XRD (PANalytical X'Pert powder diffractometer) was used to determine the crystal structure of the as-prepared active materials, corresponding to the test conditions of the Cu-Kα source. Raman spectroscopy (Renishaw RM2000) was used to determine the defects of carbon materials by measuring the change in scattered light frequency relative to incident light frequency. XPS (Thermo Scientific ESCALAB 250Xi) was used to determine the chemical state and composition, utilizing X-ray photons to stimulate the inner electrons of the sample. Nitrogen physical isothermal adsorption and desorption curves (Micromeritics ASAP 2460) were used to obtain the SSA and pore size distribution by using the Brunauer–Emmett–Teller (BET) equation, t-plot method, and density functional theory (DFT).

Fabrication of lithium-ion capacitor: The active electrode of the lithium-ion capacitor was fabricated using the active substances, conductive agent (Super C45) and binder (PVDF), and the mass ratio of N-PC electrode and T–Nb₂O₅ electrode was 85:10:5 and 75:20:5, respectively. Firstly, the evenly dispersed slurry was coated on the aluminum foil, and the as-prepared electrode was dried at 120 °C for 12 h. Then, the circular electrode pieces with a diameter of 10 mm were compacted by a powder tablet press under a pressure of 7 MPa, ensuring excellent contact between the active substance and current collector. Sequentially, the T–Nb₂O₅ electrode assembled into a lithium-ion battery was stopped after three periods of charge and discharge at a current density of 0.1 A g⁻¹. Then, the pre-lithiated T–Nb₂O₅ electrode was detached into the glove box. After that, the lithium-ion capacitor was assembled using the pre-lithiated T–Nb₂O₅ electrode, polypropylene separator, an N–PC electrode, and 1 M LiPF₆ electrolyte (ethylene carbonate/dimethyl carbonate/diethyl carbonate, 1:1:1 volume ratio) through the match of anode charges and cathode charges in glove boxes protected by an inert atmosphere. Finally, the CV and EIS were tested by using an CHI660E, and the GCD was measured using the Neware test system.

The energy density of the lithium-ion capacitor (E, Wh kg^{-1}) was calculated using Equation (4), as follows:

$$E = \frac{\int U dq}{3.6m} \tag{4}$$

where U (V) is the potential, q (C) is the charge quantity, and m (g) is the sum of the anode and cathode active substances.

The power density of the lithium-ion capacitor (P, W kg⁻¹) was calculated using Equation (5), as follows:

$$P = \frac{L}{t} \times 3600 \tag{5}$$

where *E* (Wh kg⁻¹) is the energy density, and *t* (s) is the discharge time.

C

The capacity of the lithium-ion capacitor (C, mAh g^{-1}) was calculated using Equation (6), as follows:

$$C = \frac{2I\int Udt}{3.6mV} \tag{6}$$

where I (A) is the discharge current, U (V) is the potential, t (s) is the discharge time, m (g) is the sum of the anode and cathode active substances, and V (V) is the discharge potential.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/nanoenergyadv2040016/s1, Figure S1: Typical SEM images of the porous carbon showing the smooth and discontinuous pore structure. Figure S2: Typical TEM images of the porous carbon (PC) and N-doped porous carbon (N-PC). Figure S3: Physical characterizations of PC and N-PC. Figure S4: TEM images of the Nb₂O₅ prepared at different reactive temperatures. Figure S5: Typical SEM images of N-PC with three-dimensional skeleton structure and rough surface. Figure S6: Raman spectrum of PC and N-PC. Figure S7: SEM images of the Nb₂O₅ prepared at different reactive temperatures. Figure S8: Physical characterizations of PC and N-PC. Figure S9: CV curves of (a) PC and (b) N-PC at different scan rates. Figure S10: Electrochemical properties of N-PC cathode. Figure S11: Electrochemical properties of Nb₂O₅-600, Nb₂O₅-700 and Nb₂O₅-800. Table S1: Analysis of the fitted N1s peaks from XPS. Table S2: Analysis of the fitted C1s peaks from XPS. Table S3: Analysis of the fitted O1s peaks from XPS. Table S4: Porosity parameters of PC and N-PC.

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