One-dimensional bunched Ni-V₂O₃@C@CNT for superior performance lithium-ion batteries and hybrid capacitors

Youcun Bai

Department of Applied Chemistry, College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 401331, P. R. China

Abstract

In this paper, by using the bamboo-like carbon nanotubes (BCNTs) from sulfonated polymer nanotubes (SPNTs), the 3D porous sugar-coated haws stick-like composites decorated with V₂O₃ and Ni nanoparticles (NV@C@CNT) have been prepared via a facile solution method and subsequent annealing reactions. The porous carbon matrix derived from the SPNTs provides a continuous highly conductive network to facilitate the fast charge transfer and form a stable solid electrolyte interface film. This engineering protocol toward electrode architectures/configurations endows integrated NV@C@CNT anodes with large specific capacity (895.6 mAh g⁻¹ at 0.2 A g⁻¹ after 100 cycles), good operation stability, excellent rate capabilities, and prolonged cyclic life span. To prove their potential real applications, we have established the NV@C@CNT//FCNT lithium ion capacitors (LICs), which is capable of showing high energy densities, power densities, and long cycle stability. This work provides a scalable, simple, and efficient evolutionary method for the production of NV@C@CNT electrode materials, providing useful inspiration and guidance for the anodic applications of metal oxides in next-generation power sources.

KEYWORDS

CNT, Energy densities, Li-ion capacitors, Ni-V2O3, Sandwich-like

1 | INTRODUCTION

In recent years, with the continuous growth of energy demand, the energy crisis has become increasingly prominent. Therefore, the current focus of attention is the environmental protection of renewable solar cells, lithium-ion batteries (LIBs), supercapacitors (SCs), and so on.¹,² Among them, LIBs and SCs have been widely studied due to their excellent electrochemical properties such as high energy density and high power density, respectively.³ However, LIBs and SCs alone cannot meet the higher electrochemical performance and safety requirements of modern intelligent devices. As a new type of energy storage device, lithium-ion capacitors (LICs) combines the advantages of LIBs and SCs, which is expected to fill the gap between the two systems, this leads to the desire to the development of new devices with more balanced energy storage performance.⁴ To develop cost-competitive LICs, it is crucial to find low cost and high-performance anode and cathode materials, especially considering the scale of the entire technology from synthesis, manufacture to the application and...
solving the energy storage dynamic imbalance between anode and cathode electrodes. Therefore, finding suitable electrode materials to overcome the above problems is one of the major challenges for the LICs field.

In recent years, a great deal of research has been done on the development of new electrode materials. The ideal anode material for LIBs should meet the requirements of low redox potential and high output voltage, and be able to embed more lithium ions. At the same time, the insertion/extraction of lithium ions is reversible and the structure is unchanged in the electrochemical reaction process. Besides, electrode materials should have high ionic/electronic conductivity, low cost, no pollution, and other requirements. Surprisingly, V$_2$O$_3$ not only has a high theoretical capacity (1070 mAh g$^{-1}$) but also has an internal tunnel structure provided by the V-V skeleton, providing abundant Li$^+$ embedding sites, which is considered as a potential electrode material have been favored by researchers. Obviously, V$_2$O$_3$ also has the same disadvantages as other transition metal oxides, such as poor conductivity, easy agglomeration and volume expansion. Compounding with highly conductive carbon materials is an effective way to solve the above problems. Therefore, sugar-coated haws stick-like were designed using bamboo-like carbon nanotube with a strong skeleton and carbon with good electrical conductivity to improve the electrochemical properties of the electrode. Furthermore, the studies conducted that the transition metal nanoparticles like Ni not only improves electrical conductivity but also can work as electrochemical catalysts for the reversible formation/decomposition of some solid electrolyte interface (SEI) components and hence present a certain electrochemical capacity. Hence, in this paper, the introduction of Ni leads to the formation of Ni/V$_2$O$_3$ structures, which are expected to exhibit better electrochemical performance than single components.

As is known to all, carbon material has been widely studied as the cathode material of the capacitor, and it is urgent to prepare porous carbon material with excellent adsorption and desorption properties. Therefore, in this paper, the electrochemical performance of LICs is improved through activated CNT by potassium hydroxide $\text{KOH}$, which is an effective strategy to improve the dynamic imbalance between anode and cathode.

Based on the considerations above, we have synthesized a new type of LICs by utilizing NV@C@CNT as a battery-type anode and FCNT as a capacitor-type cathode. At the same time, a series of comparative materials were synthesized. The hybrid LICs provide high energy densities of 144.8 and 93.6 Wh kg$^{-1}$ at power densities of 375 and 10,015.7 W kg$^{-1}$, respectively. Hopefully, the results of this study will rekindle the interest of researchers that this unique structure applies not only to hybrid LICs but also to future energy conversion and storage applications.

**HIGHLIGHTS**

1. Synergistic effect of Ni and V$_2$O$_3$ makes the material exhibit excellent electrochemical properties.
2. Sugar-coated haws stick-like electrode with highly conductive CNT has superior performance.
3. LIC showing high energy densities, power densities, and long cycle stability.

### EXPERIMENTAL SECTION

Scheme 1 shows the schematic of the fabrication process for cathode and anode materials as well as the energy storage mechanism of LICs. In brief, NV@C@CNT was prepared by stirring and the following carbonization process. Additionally, the cathode was obtained by simple chemical activation of CNT with KOH as an active agent. Ultimately, the novel LICs is constituted, which can integrate the advantages of battery and supercapacitor. For the NV@C@CNT//FCNT LIC, the PF$_6^-$ ions were absorbed on the surface of the FCNT cathode during the charging process, indicating a capacitive behavior. Whereas Li$^+$ ions were intercalated into the nanoplate or absorbed on the surface of NV@C@CNT anode, suggestive of a battery-type nature. The discharge process is reversed. The above demonstrates the synergistic use of capacitor and battery elements.

The main advantages of our NV@C@CNT//FCNT LIC over previously reported Li-ion capacitors are as follows: (1) For the anode material, the CNT with high flexibility in the NV@C@CNT can effectively reduce the mechanical stress during lithiation/delithiation, resulting in excellent cycle stability. (2) The abundant Ni in NV@C@CNT can improve its electronic conductivity and electrochemical reactivity, and provide active sites for Li$^+$ intercalation/deintercalation, thereby improving the specific capacity and rate capability; (3) In the cathode, the high surface area and numerous nanopores of FCNT can provide a large electrode/electrolyte interface, which promotes rapid charge transfer and PF$_6^-$ adsorption/desorption; (4) Both the anode and the cathode have the carbon nanotube structure, which reduces the diffusion resistance during charge and discharge. In addition, the synergistic effect of NV@C@CNT and FCNT can effectively improve the power density and energy density.
RESULTS AND DISCUSSION

3.1 Material characterization

XRD patterns of the NV@C@CNT, V@C@CNT, NV@CNT, and NV@C samples are shown in Figure 1A. The diffraction peaks of the four samples were consistent with those of V_2O_3 (JCPDS 34–0187), indicating V_2O_3 has been synthesized successfully. The main peaks located at 2θ = 24.3, 32.9, 36.2, 41.2, 49.8, 53.9, 63.1, and 65.2° can be attributed to the (012), (104), (110), (113), (024), (116), (214), and (300) planes of V_2O_3.[21] Besides, the XRD patterns of the NV@C@CNT, NV@CNT and NV@C samples also show the diffraction peaks of Ni (JCPDS 04–0850), indicating that the three samples are composed of V_2O_3 and Ni. Fig. S1 shows the XRD pattern of the FCNT, in which two obvious peaks at 24.4° and 44.2° correspond to (002) and (100) facets of CNT, respectively.[22]

Besides, EDS and element mapping were used to further study the composition of the NV@C@CNT, V@C@CNT, NV@CNT, and NV@C samples. Fig. S2 shows EDS spectra and corresponding elemental mappings of NV@C@CNT. It can be seen that they present a uniform distribution in the NV@C@CNT sample, indicating the successful preparation of Ni-V_2O_3@C@CNT nanocomposite. EDS spectra reveal V@C@CNT (Fig. S3b-g), NV@C (Fig. S4b-h), and NV@CNT (Fig. S5b-h) have similar O, N, C, Ni, and V elements and are uniformly distributed. Besides, the graphitization degree of the samples was determined by testing the Raman scattering spectra of NV@C@CNT, V@C@CNT, NV@CNT and NV@C samples. As shown in Figure 1B, there are two typical peaks at 1356 and 1587 cm⁻¹, which belong to the D and G bands of carbonic materials, respectively.[22] The I_D/I_G value of NV@C@CNT, V@C@CNT, NV@C and NV@CNT and was calculated are 0.95, 1.15, 1.02, and 1.14, indicating the more disorder carbon in the NV@C@CNT.[20,22] Thermogravimetric analysis (TGA) under air is applied to calculate the content of Ni and V_2O_3 in the NV@C@CNT, as shown in Figure 1C.

Thermal degradation involved two steps. The slight weight loss before 200°C was ascribed to the evaporation of absorbed water. Dramatic weight losses could be seen at about 300°C, which is assigned to the consumption of carbon and the oxidation of Ni and V_2O_3.[21] it can be seen from Figure 1D that NV@C@CNT is oxidized into NiV_2O_6 in the air. The final weight percentages of NiV_2O_6 are about 44.3% (Figure 1C). The transformation process can be described by the following reactions:

\[
\text{Ni} + \text{V}_2\text{O}_3 + 3/2\text{O}_2 = \text{NiV}_2\text{O}_6
\] (1)

Thus, the weight percentages of Ni and V_2O_3 are 10.2 and 25.8% for NV@C@CNT, respectively.

The surface chemical constituents and bonding states of NV@C@CNT, V@C@CNT, NV@CNT and NV@C were characterized by X-ray photoelectron spectroscopy (XPS). As can be seen from Figure 2A, the XPS spectrum clearly shows the presence of major elements V, Ni, C, N, and O. The high-resolution V 2p spectrum of NV@C@CNT, V@C@CNT, NV@CNT and NV@C are displayed in Figure 2B, which can be distinguished into V 2p_3/2 and 2p_1/2 signals. The peaks at 516.5 and 523.8 eV belong to V^{3+}, and the two peaks at 517.2 and 524.9 eV are ascribed to V^{4+}.[23] Meanwhile, the V 2p signals in NV@CNT was the weakest among the four samples due to the low content of vanadium.[24] Figure 2C displays the O 1s spectra of the four samples, in which the peak at 529.7 eV is attributed to Ni-O, and the peaks at 530.5 eV and 532.2 eV are assigned to lattice O and adsorbed water, respectively,[25] while the main bonding states of in these samples is Ni-O due to the
presence of a greater amount of Ni.\[16\] Figure 2D shows the high-resolution Ni 2p spectra of NV@C@CNT, NV@C and NV@CNT. The two major peaks located at 855.9 and 873.5 eV can be ascribed to Ni 2p3/2 and Ni 2p1/2, respectively, which is in good agreement with the Ni2+, and the two broad peaks at 861 and 879.5 eV are the satellite peaks, around 852.5 eV can be ascribed to Ni0.\[24\] The C 1s spectra of NV@C@CNT, NV@C, NV@CNT and V@C@CNT are shown in Figure 2E. The peak at 284.3 eV can be attributed to sp2-bonded carbon (C–C) of graphite carbon, and the remaining peaks at 284.9, 286 and 288.8 eV can be assigned to the C–O, C–OH and C = O bonds, respectively.\[25\] The C elements in the samples come from the BCNT and 1,10-Phenanthroline. The N 1s spectra of four samples are shown in Figure 2F, the peak in the 398.9 eV is the C–N bond and at 400.1 eV belongs to graphitic N.\[24\]

The SEM images of NV@C@CNT is shown in Figure 3. As shown in Figure 3A, the carbon nanosheets were evenly and fully coated on the outer wall of the CNTs, no serious agglomeration is observed, more significantly, carbon nanosheets are loaded with a lot of nanoparticles (Figure 3B), which is extremely important for improving the electrochemical performance of the composite. Also, SEM images of V@C@CNT, NV@C and NV@CNT are shown in Fig. S3a, Fig. S4a, and Fig. S5a. We can see from Fig. S3a, only a small amount of nanoparticles and carbon are wrapped around the CNTs in the absence of Ni, this means that Ni is more likely to coordinate with 1,10-Phenanthroline. However, according to XRD results (Figure 1A), V@C@CNT contains strong diffraction peaks of V2O5, which can be inferred that a large number of vanadium compounds enter the carbon nanotubes lumen. Besides, we can see from Fig. S4a, the nanoparticles are heavily bound to carbon without the support of the CNT. The CNT outer wall of NV@CNT is smooth (Fig. S5a), this further suggests that in the absence of a 1,10-Phenanthroline, the nanoparticles are more likely to be into the interior of the CNT. The SEM image of FCNT
FIGURE 2  XPS spectra of NV@C@CNT, NV@C, NV@CNT and V@C@CNT: full spectra (A), V 2p (B), O 1s (C), Ni 2p (D), C 1s (E), N 1s (F)
is shown in Fig. S6, its surface is smooth, compared with CNT, there is no obvious difference in morphology.

To further study the nanostructure of the NV@C@CNT composite, TEM, HRTEM, and SAED images are shown in Figure 3. As shown in Figure 3C, carbon nanosheets were evenly coated on the outer wall of the CNTs, as shown by the green and red arrows. At the same time, there are also nanoparticles in the cavities and walls of carbon nanotubes (Figure 3D), and the diameter of the CNT is ca. 100–120 nm. The nanoparticles in the cavity (blue circle) were further characterized by HRTEM (Figure 3E), it is wrapped in amorphous carbon and display obvious lattice spacings of 0.14 nm, which can be indexed to the (300) facet of V$_2$O$_5$.[26] In addition, the nanoparticles loaded on the carbon nanosheet were also characterized by TEM, a large number of nanoparticles of various sizes are embedded in the carbon nanoparticles, as shown in yellow and blue circles (Figure 3F), at the same time, its HRTEM image is shown in Figure 3 G-H. We can see that the nanoparticles (circled by two colors in Figure 3F) show different crystal lattice spacing, in which the blue line represents V$_2$O$_5$ and the yellow line represents Ni, lattice spacings of 0.27 and 0.205 nm, which is assigned to the (104) and (202) crystalline plane of V$_2$O$_5$.[26] respectively. The crystal lattice spacing 0.203 and 0.18 can point to the (111) and (200) crystalline plane of Ni.[27] Besides, we can find that the lattice spacing of the nanoparticles (circled by the yellow color in Figure 3F) is 0.18 nm, which is assigned to the (200) crystalline plane of Ni.[27] The selected area electron diffraction (SAED) pattern of the NV@C@CNT composite is shown in Figure 3I, which reveals the presence of (104), (202), and (300) lattice planes, corresponding to the
Anode performance in half-cell

Figure 4A shows the first three-cycle and tenth cycles of galvanostatic charge/discharge curves tested on NV@C@CNT at 0.2 A g⁻¹ within a potential window of 0.01–3.0 V. Meanwhile, the charge-discharge curves of NV@C, NV@CNT and V@C@CNT tested under the same conditions are shown in Fig. S7 (a, c, e). The initial discharge and charge specific capacities of the NV@C@CNT composite electrode are 1110 and 754.8 mAh g⁻¹, respectively, resulting in Coulombic efficiency of 68%. This irreversible capacity loss can be ascribed to the solid electrolyte interphase (SEI) layer. [28] The irreversible capacity loss can be ascribed to the formation of an SEI film. [30] Figure 4B shows the cyclic voltammograms (CVs) of the NV@C@CNT composite for the first three-cycle at a scan rate of 0.1 mV s⁻¹, four charge-discharge platforms similar to the redox peaks potential in GCD curve were observed, located at 2.41/1.52 V, 2.11/1.48 V, 1.84/1.1 V, and 1.15/0.7 V Li⁺/Li, respectively, which is the characteristic of Li⁺ insertion/extraction into Ni/V₂O₃. [29] Meanwhile, the CVs of NV@C, NV@CNT, and V@C@CNT are shown in Fig. S7 (b, d, f), they have similar redox peaks as NV@C@CNT. The reduction peak at 0.7 and 1.1 V of the first cathodic scan and disappeared in the subsequent cycles, which may be attributed to the formation of an SEI film. [30] Furthermore, from the second cycle onward, the CV curves are almost overlapping, indicating the electrochemical stability of the sample. And the reduction peak that appeared at approximately 1.48 and 1.52 V, which can be attributed to the reduction of V⁵⁺ into V⁰. [30] In the anodic scans, the anodic peak at 2.11 V (vs. Li/Li⁺) corresponds to the conversion of Ni to NiO and the decomposition of Li₂O to Li⁺ (Ni+Li²O→NiO+2Li⁺+2e⁻). [26,31] Diverse peaks on the CV curves correspond to different states of reactions. The electrochemical reaction mechanism of the V₂O₃ electrode may be as follows in Eqn (2) and (3):[31]

\[ \text{V}_2\text{O}_3 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{V}_2\text{O}_3 \]  

(2)

\[ \text{Li}_x\text{V}_2\text{O}_3 + (6 - x) \text{Li}^+ + (6 - x)e^- \leftrightarrow 2\text{V} + 3\text{Li}_2\text{O} \]  

(3)

Figure 4C shows the electrochemical impedance spectra (EIS) of NV@C@CNT, V@C@CNT, NV@C and NV@CNT, the charge transfer resistance Rₜ value NV@C@CNT, V@C@CNT, and NV@C are 138, 344, and 425 Ω, respectively, however, the Rₜ value of NV@C@CNT only is 136 Ω, indicating that the composite of NV@C@CNT can more effectively improve the conductivity of the material, facilitate the transmission of electrons and lithium ions, and improve the electrochemical property. [32] Figure 4D shows the cycle performances of NV@C@CNT, V@C@CNT, NV@C, and NV@CNT composites at 0.2 A g⁻¹. Meanwhile, the cycling performance of CNT has been reported in our previous work. [13] The specific capacities of NV@C@CNT, V@C@CNT, NV@C, and NV@CNT are 895.6, 475.1, 259.7, and 645.3, respectively, all the samples showed excellent specific capacity. The specific capacity of NV@C@CNT is the highest among all composites under the same conditions, this demonstrated the importance of CNT (NV@C@CNT > NV@C), Ni (NV@C@CNT > V@C@CNT) and C (NV@C@CNT > NV@CNT) in the energy storage of NV@C@CNT, besides, the specific capacities of the pristine CNT much is lower than those of the composite under the same condition, it is inferred that this is due to the synergistic effect of the components. Importantly, the specific capacity of NV@C@CNT decreased only in the first few cycles, and then remained stable, after 100 cycles, the specific capacity remained at 895.6 mAh g⁻¹. In summary, the excellent electrochemical performance of the NV@C@CNT electrode is mainly attributed to this unique sugar-coated haws stick-like. As a result, not only effectively prevented the aggregation, fragmentation, and deactivation of nanoparticles, but also improved the conductivity and structural stability of the composites due to the existence of CNT and C, at the same time, the synergistic effect of Ni and V₂O₃ with high theoretical capacity improves the electrochemical performance of the NV@C@CNT composites. The rate performances of NV@C@CNT, V@C@CNT, NV@C, and NV@CNT are shown in Figure 4E,F, it was found that the discharge capacity of NV@C@CNT reached 838.2, 637.5, 486.8, 373.1, 323.1, 289.4, and 184.7 mA h g⁻¹ at 0.2, 0.5, 1, 2, 3, 5, and 8 A g⁻¹, respectively. When the current density return to 0.2 A g⁻¹, the specific capacity is 724.7 mAh g⁻¹, which is still much higher than those of V@C@CNT, NV@C, and NV@CNT at the same current densities. The NV@C@CNT composite has the best rate property, it is because the unique structure of the composite can shorten the diffusion path of Li⁺ and electrons. At the same time, BCNT and C in nanocomposites are a rigid skeleton bearing electroactive metal oxides for Li⁺ insertion/extraction, which can effectively mitigate the structure/volume changes in the electrochemical process. Also, Ni can reversibly form/decompose some SEI components to improve electrochemical performance. [9,16,17] As shown in Figure 4G, the specific capacity of the NV@C@CNT electrode up to 309.1 mAh g⁻¹ after 1900 cycles at 5 A g⁻¹, Coulombic efficiency is almost 100%. Furthermore, as shown in Figure 4H and Table S2, we found that the performance of NV@C@CNT in a half cell
FIGURE 4 The electrochemical performances of anode: Charge-discharge profiles at 0.2 A g\textsuperscript{-1} (A), CVs at 0.1 mV s\textsuperscript{-1} (B), Impedance plots of NV@C@CNT, V@C@CNT, NV@C, and NV@CNT (C), cycle performances (D), rate performances (E), charge-discharge profiles of NV@C@CNT at different current densities (F), and long cycle performance and Coulombic efficiency of NV@C@CNT at 5 A g\textsuperscript{-1} (G), cycle performances of some V\textsubscript{2}O\textsubscript{5} matrix composites reported in the literature (H)
is better than some V$_2$O$_3$ matrix composites reported in the literature.$^{[26,31–38]}$

Ex-situ XRD was performed to illustrate the structural change of NV@C@CNT after the cycle process. It can be seen from Fig. S8, there is no new phase generation in the XRD peak after cyclic testing, and the (111) peak of Ni and (110) peak of V$_2$O$_3$ are greatly reduced, this indicates that the charge and discharge cycle reduces the crystallinity of the sample. The SEM image of NV@C@CNT after the 1900 cycles is shown in Fig. S9. It can be found that most of the carbon nanosheets have been detached from the surface of the CNT. However, CNT remains intact, which helps to keep the nanoparticles active in the lumen and the wall of the tube during the cycling process, therefore, it shows excellent cyclic stability.

XPS measurements were also performed to determine the surface chemical constituents and bonding states of the NV@C@CNT nanosheets after the 1900 cycles. Compared to the full spectrum before the cycle, a distinct peak of F was observed after the 1900 cycles (Fig. S10a), this is mainly from the electrolyte. The XPS spectrum of V 2P shows two obvious peaks at 531.2, and 532 eV, which can be put down to V 2P$_{3/2}$ ($\mathrm{V^{3+}}$), and V 2P$_{1/2}$ ($\mathrm{V^{4+}}$), as shown in Fig. S10b. Meanwhile, the weak peak near 516 eV is attributed to V 2P$_{3/2}$, and is weakened by the insertion/ disinsert of lithium ions.$^{[25]}$ Fig. S10c presents three peaks of the O 1s spectrum, three peaks located at 530.8, 531.5, and 532.4 eV can be allocated to Ni-O, lattice oxygen and adsorbed oxygen, respectively.$^{[25]}$ Fig. S10d shows the XPS Ni 2p spectra of NV@C@CNT. The two major peaks located at 855.8 and 859.6 eV can be ascribed to Ni 2p$_{3/2}$, and Ni 2p$_{1/2}$, respectively.$^{[16]}$ Furthermore, the high-resolution C 1s spectrum of the composite was analyzed to confirm the bonding states. The C 1s spectrum can be fitted with six peaks (Fig. S10e). The peak at 284.1 eV represents the bond between carbon and carbon (C–C). The peak observed at 284.8 eV can be attributed to the bond between carbon and oxygen (C–O). This small peaks located at 286.4, 288.1, 289.6, and 292.8 eV indicates the C-OH, COOR, C = O, and CF$_3$ species, respectively.$^{[25]}$ N 1s spectrum is shown in Fig. S10f, in which the peak at 399.2 eV is attributed to the C-N bond.$^{[34]}$ In addition, the NV@C@CNT nanosheets after cycles contain a certain amount of F, and its 1s spectrum is shown in Fig. S10g, two strong peaks can be seen, which are located at 688 and 688.9 eV, attributed to LiF and CF$_2$, respectively.$^{[39]}$

### 3.3 Cathode performance in half-cell

The CV curve of FCNT within the potential window of 2.5-4.3 V is shown in Figure 5A, and there is no obvi-
ous redox peak, indicating that its capacitance behavior is relatively ideal.$^{[1]}$ It is obvious that the CV curve of the FCNT electrode presents rectangular shapes with slight humps under different scanning rates, indicating that the pseudo-capacitance contribution is a small part.$^{[12]}$ The charge-discharge curve of FCNT is shown in Figure 5B. The approximately linear GCD curves are consistent with the CV curves. The specific capacity of FCNT is calculated as 105.9, 99.6, 95, 84.7, and 74.8 mAh g$^{-1}$ at 0.1, 0.2, 0.5, 1, and 2 A g$^{-1}$. Importantly, the rate performance of FCNT is better than that of most reported carbon cathode materials (Figure 5C).$^{[6,42–47]}$ This is since the porous structure of FCNT can significantly promote the adsorption/desorption of PF$_6^–$ in the FCNT, thus enhancing the electrochemical performance.$^{[3,4]}$ Based on the CVs at different scan rates, the $b$ value in equation S1 can be calculated. As can be seen from Figure 5D, within the voltage range of 3-3.5 V, the value of $b$ is close to 1, while the value of $b$ is close to 0.5 on both sides of the voltage window, indicating that both diffusion and capacitive exist.$^{[6,7]}$ It is found that the capacity contribution is 50.8% at 1 mV s$^{-1}$ by calculating (Figure 5E). With the increase of the scanning rate, the capacitive contribution increases gradually (Figure 5F). As shown in Fig. S11 and Fig. S12, the specific capacity of FCNT is much higher than that of CNT under the same electrochemical performance test. After 300 cycles, the specific capacity of FCNT has maintained at 103.6 mAh g$^{-1}$, while the specific capacities of CNT are only 27.8 mAh g$^{-1}$ after 50 cycles. Besides, the specific capacity of FCNT is still as high as 70.7 mAh g$^{-1}$ after 1800 cycles even at a high current density of 2 A g$^{-1}$ (Figure 5G). This excellent electrochemical performance further proves that activation with KOH is very successful, functional groups containing O are generated through activation, which facilitates rapid charge transfer and ion adsorption/desorption,$^{[40]}$ increase additional capacitance, and make FCNT an ideal cathode material for LiCs.

### 3.4 Electrochemical performance of the NV@C@CNT//FCNT LIC

The LIC is assembled with NV@C@CNT as anode and FCNT as a cathode. To obtain a highly efficient pre-lithiated state, before the LIC was assembled, the NV@C@CNT electrode was pre-activated in a half-cell at 0.1 A g$^{-1}$ from 3.0 to 0.01 V vs Li$^+$/Li for 6 cycles. The preactivation treatment of anodes can activate the materials, and reduce side reactions including the formation of SEI.$^{[1]}$ Figure 6A shows the configuration of the NV@C@CNT//FCNT LIC device. It can be seen that the charge storage process is completed by the redox reaction involving Li$^+$ ion at the anode electrode and the
FIGURE 5 The electrochemical performances of cathode maters: CV curves at various scan rates (A) and charge-discharge profiles at different current densities of FCNT (Bb), rate performances of FCNT and some carbon cathodereportedintheliterature(C),the $b$-values of FCNT at different measured potentials (D), CV at 1 mV s$^{-1}$ with capacitive and diffusion-controlled contributions (e), contribution ratio of the capacitive and diffusion-controlled charge at differentscan rates (F), and long cycle performance of FCNT at 2 A g$^{-1}$ (G).

adsorption/desorption of PF$^-$ ion at the cathode electrode. Therefore, the LIC device combines the battery type behavior of NV@C@CNT electrode and the capacitive behavior of FCNT. As shown in Figure 6B, at a high current density, the LIC charge-discharge curves in the range of 1.0 $\sim$ 4.0V presents a symmetrical quasitriangular shape, indicating the combination of different storage mechanisms.$^{[2]}$ And the specific capacitance of LICs can reach 45 F g$^{-1}$ even at the high current density of 4 A g$^{-1}$. As shown in Figure 6C, a series of CV experiments was carried out at different scanning speeds, and it was found that the rectangular shape was more ideal with the reduction of scanning speed. Figure 6D shows the trade-off between energy and power density of the present NV@C@CNT//FCNT LICs. A high-energy-density of 144.8 Wh kg$^{-1}$ is achieved at a power density of 375 W kg$^{-1}$. Even at a high power density of 10,015.7 W kg$^{-1}$, the LIC still delivers an energy density of 93.6 Wh kg$^{-1}$. This ultrahigh energy and power performance of the NV@C@CNT//FCNT LICs is superior to those of most of the previously reported LICs (Figure 6D and Table S3)$^{[41,42,44,47-51]}$ The exhibit excellent electrochemical
performance of LICs is mainly due to the following reasons. Firstly, the nanostructural Ni-V$_2$O$_3$@C@CNT anode possessed both high porosity and conductivity, leading to fast electron/ion transfer. Secondly, the hierarchical NV@C@CNT nanostructure can well solve the volume change problem of the conversion reaction anode, which makes the anode and LICs devices have good reversibility. Finally, during adsorption/desorption, nanoscale porous carbon reduces the length of the ion transport path at the cathode and increases the number of electrolyte ions near the electrode surface. Therefore, excellent electrochemical performance was obtained. As shown in Figure 6E, the cycling stability of the NV@C@CNT//FCNT LICs is investigated at the current density of 4 A g$^{-1}$, and the device maintains its capacity retention of 80.1% up to 3000 cycles. This work demonstrates that a high-performance electrode of LICs device can be achieved through reasonable material design and control.

4 | CONCLUSIONS

In summary, we have developed a new type of LIC with NV@C@CNT as anode and FCNT as the cathode. The obtained NV@C@CNT anode with favorable architectures yielded excellent lithium storage property, delivering a high capacity of 895.5 mAh g$^{-1}$ at a current density of 0.2 A g$^{-1}$. The high level of activation with abundant capacitive charge storage contributions in the FCNT cathode, which show an excellent specific capacity of 70.7 mAh g$^{-1}$ after 1800 cycles at a current density of 2 A g$^{-1}$. This hybrid NV@C@CNT//FCNT device exhibited superior electrochemical properties in terms of a maximum energy density of 144.8 Wh kg$^{-1}$ and a maximum power density of 10,015.7 W kg$^{-1}$, and with 80.1% capacitance retention after 3000 cycles. Therefore, the nanomaterials developed in this paper can be an ideal candidate for energy storage.

The research results of this paper provide a certain basis for the material selection and structure design of high-performance LIC, and lay a good foundation for the next generation of energy storage technology with high energy density and power density.

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CONFLICTS OF INTEREST
The authors declare no competing financial interest.

DATA AVAILABILITY STATEMENT
Research data are not shared.

ORCID
Youcun Bai https://orcid.org/0000-0001-8189-6117

REFERENCES
1. H. D. Liu, Z. Y. Zhu, Q. Z. Yan, S. C. Yu, X. He, Y. Chen, R. Zhang, L. Ma, T. C. Liu, M. Li, R. Q. Lin, Y. M. Chen, Y. J. Li, X. Xing, Y. J. Choi, L. Gao, H. S. Cho, K. An, J. Feng, R. Kosteecki, K. Amine, T. Wu, J. Lu, H. L. Xin, S. P. Ong, P. Liu, Nat. 2020, 585, 63.
2. C. Yue, M. Y. Wu, B. S. Cheng, M. Dang, G. Z. Liu, F. Hu, J. Li, Adv. Mater. Interfaces 2020, 2001043.
3. S. Jeong, I. Lee, T. S. Kim, J. Y. Lee, Adv. Mater. Interfaces 2020, 2001425.
4. Z. P. Xu, Y. Huang, Z. Zhang, L. Ding, H. Gao, T. H. Li, Ceram. Int. 2020, 46, 25775.
5. Z. Xu, F. Xie, J. Wang, H. Hu, M. Tebyetekerwa, Z. Y. Guo, S. Y. Yang, Y. S. Hu, M. M. Titirici, Adv. Funct. Mater. 2019, 29, 1903895.
6. T. Liang, H. W. Wang, R. X. Fei, R. Wang, B. B. He, Y. S. Gong, C. J. Yan, Nanoscale 2019, 11, 20715.
7. J. M. Jiang, J. R. Yuan, P. Nie, Q. Zhu, C. L. Chen, W. J. He, T. F. Zhang, H. Dou, X. G. Zhang, J. Mater. Chem. A 2020, 8, 3956.
8. H. Zheng, Q. Zhang, H. Gao, W. Sun, H. M. Zhao, C. Q. Feng, J. F. Maoc, Z. P. Guo, Energy Storage Mater. 2019, 22, 128.
9. K. Y. Tao, Y. Gong, J. H. Lin, Nano Energy 2019, 55, 65.
10. F. Sharifianjazi, M. faMoradi, N. Parvin, A. Nemati, A. Jafari-Rad, N. Sheysi, A. Abouchenari, A. Mohammadi, S. Karbasi, Z. Ahmadi, A. Esmaeilionkhanian, M. Irani, A. Pakseresht, S. Sahmani, M. S. Asl, Ceram. Int. 2020, 46, 18391.
11. L. C. Meng, R. S. Guo, F. Y. Li, Y. L. Ma, J. H. Peng, T. T. Li, Y. Luo, Z. Y. Li, X. H. Sun, Energy Technol. 2020, 8, 1900986.
12. H. Y. Wu, Z. Y. Zhang, M. L. Qin, Q. Y. Wang, Z. Q. Cao, Y. Yuan, B. R. Jia, X. H. Qu, J. Am. Ceram. Soc. 2019, 12, 2643.
13. Y. C. Bai, Y. K. Tang, L. Liu, X. H. Li, Y. Gao, ACS Sustainable Chem. Eng. 2018, 6, 41614.
14. H. Zhang, Y. S. Wang, W. Q. Zhao, M. C. Zou, Y. J. Chen, L. S. Yang, L. Xu, H. S. Wu, A. Y. Cao, ACS Appl. Mater. Interfaces 2017, 9, 37813.
15. Y. C. Dong, K. Md, Y. S. Chui, Y. Xia, C. W. Cao, J. M. Lee, J. Z. Zapien, Electrochim. Acta 2015, 176, 1332.
16. C. C. Yang, D. M. Zhang, L. Du, Q. Jiang, J. Mater. Chem. A: J. Mater. Chem. 2018, 6, 12663.
17. I. Elizabeth, A. K. Naird, B. P. Sing, S. Gopukumara, Electrochim. Acta 2017, 23098.
18. Z. Q. Hu, X. F. Xu, X. F. Wang, K. F. Yu, C. Liang, J. Alloys Compd. 2020, 835, 155446.
19. N. F. Zhou, W. Qin, C. Wu, C. K. Jia, J. Alloys Compd. 2020, 834, 155073.
20. R. Fang, W. Xiao, C. Miao, P. Mei, X. M. Yan, Y. Zhang, Y. Jiang, J. Alloys Compd. 2020, 834,155230.
47. C. P. Han, R. Y. Shi, D. Zhou, H. F. Li, L. Xu, T. F. Zhang, J. Q. Li, F. Y Kang, G. X. Wang, B. H. Li, *ACS Appl. Mater. Interfaces* **2019**, *11*, 15646.
48. L. F. Shen, H. F. Lv, S. Q. Chen, P. Kopold, P. A. van Aken, X. J. Wu, J. Maier, Y. Yu, *Adv. Mater.* **2017**, *29*, 1700142.
49. Y. Sun, J. P. Ma, X. Y. Yang, L. P. Wen, W. D. Zhou, J. X. Geng, *J. Mater. Chem. A* **2019**, *8*, 62.
50. J. M. Jiang, Y. D. Zhang, Y. F. An, L. Y. Wu, Q. Zhu, H. Dou, X. G. Zhang, *Small Methods* **2019**, 1900081.
51. S. J. Huang, L. W. Yang, M. Gao, Q. Zhang, G. B. Xu, X. Liu, J. X. Cao, X. L. Wei, *J. Power Sources* **2019**, *437*, 226934.

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