Surfactant-Assisted Growth of a Conversion-Type Binary Metal Oxide-Based Composite Electrode for Boosting the Reversible Lithium Storage

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ABSTRACT: High-performance anode materials play a crucial role in paving the development of next-generation lithium-ion batteries (LIBs). NiCo$_2$O$_4$, as a typical binary metal oxide, has been extensively demonstrated to possess higher capacity and electrochemical activity compared with a monometal oxide such as NiO or Co$_3$O$_4$. However, the advances in the application of LIBs are usually limited by the relatively low electrical conductivity and large volume change during repeated charging/discharging processes. Herein, a NiCo$_2$O$_4$@carbon nanotube (CNT) composite electrode with advanced architecture is developed through a facile surfactant-assisted synthetic strategy. The introduced polyvinyl pyrrolidone can greatly facilitate the heterogeneous nucleation and growth of the NiCo precursor on CNTs and thus benefit the uniform transformation to a well-confined NiCo$_2$O$_4$@CNT composite. The CNTs combined with NiCo$_2$O$_4$ tightly act as both a conductive network for enhancing the ion/electron transfer and a support for mitigating the volume expansion of NiCo$_2$O$_4$. As a result, the NiCo$_2$O$_4$@CNT electrode exhibits a high initial capacity of 830.3 mA h g$^{-1}$ and a good cycling stability of 608.1 mA h g$^{-1}$ after 300 cycles at 2000 mA g$^{-1}$.

INTRODUCTION

With the increasing environmental pollution and energy crisis caused by the rapid consumption of fossil fuels, numerous efforts have been made to develop clean and renewable energy systems. Lithium-ion batteries (LIBs), as one of the dominant energy storage and conversion devices in current society, are widely applied in electronic devices and vehicles because of their relatively high energy density, excellent cyclability, long life span, and environmental friendliness. The properties of electrode materials greatly influence the performance of LIBs. Therefore, the design of appropriate anode materials is of prime importance to realize the advantages of LIBs. Typically, anode materials are mainly categorized into three types, that is, intercalation-, alloying-, and conversion-based anodes, according to their reaction mechanisms in LIBs. Most intercalation-type anode materials suffer from low theoretical capacities. For example, graphite has limited Li intercalation capacity (LiC$_6$, 372 mA h g$^{-1}$) and poor rate performance because of the low Li diffusion coefficient in the graphite lattice. Alloying-based anode materials (such as Sb, Zn, In, Si, and Cd) typically perform the alloying reaction with lithium and possess extremely high practical reversible capacities (800−1800 mA h g$^{-1}$) and low working potentials. Unfortunately, alloying-based anode materials usually have large volume variation during the cycles and high cost because of their non-natural form. Conversion-based anode materials based on the replacement redox reactions between Li$^+$ and transition-metal cations generally have high theoretical capacities. Meanwhile, in comparison with graphite anodes, conversion-based anode materials exhibit better security of LIBs via avoiding the formation of lithium dendrite. In addition, many conversion-based anode materials usually exist in their natural forms which possess relatively low cost. Thus, conversion-based anode materials with higher capacity and better security than intercalation-type materials.
NiCo$_2$O$_4$ with conductive substrates [such as carbon nanotubes (CNTs)] is another well-known method to combine anode materials delivering a capacity of 1020 mA h g$^{-1}$ at 1000 mA g$^{-1}$ after 300 cycles. However, because of the poor electrical conductivity and toxicity of cobalt, many efforts have been made to partially replace Co$_2$O$_4$ with other eco-friendly metal oxide materials. Recently, binary metal oxide NiCo$_2$O$_4$ has drawn extensive attention as an alternative electrode material owing to its multiple redox reactions and a high theoretical capacity of 891 mA h g$^{-1}$. Compared with its monometallic oxide counterparts (nickel oxides or cobalt oxides), NiCo$_2$O$_4$ possesses enhanced electrical conductivity and improved electrochemical activity. Even though, its application in LIBs is still hampered by the large volume change during repeated charging/discharging process and limited enhanced conductivity, which leads to irreversible capacity loss and inferior cycling performance.

To mitigate these issues, two types of strategies are mainly proposed to improve the electrochemical performance of NiCo$_2$O$_4$-based anode materials. One is to prepare nano-scaled NiCo$_2$O$_4$ with hollow structures such as nanoboxes, nanospheres and nanotubes, which hold the advantages to withstand volume variation and shorten the diffusion distance of lithium ions. Another well-known method is to construct NiCo$_2$O$_4$ with conductive substrates [such as carbon nanotubes (CNTs), reduced graphene oxide, and three-dimensional porous carbon matrix]. The introduced conductive substrates can not only enhance the conductivity of electrode but also maintain the structural integrity for enhanced stability upon prolonged charge/discharging cycling for LIBs. Notably, one-dimensional (1D) CNTs with superior electrical conductivity, high mechanical property, large surface area, and especially the well-defined surface lattice structure have been considered as one of the most promising supporting materials. Recently, NiCo$_2$O$_4$ nanoparticles compositied with multi-walled CNTs have been reported as anode materials delivering a capacity of 1020 mA h g$^{-1}$ at 300 mA g$^{-1}$ after 200 cycles. Besides, CNTs/NiCo$_2$O$_4$ core/shell structures synthesized via an electrochemical deposition method exhibits rate capabilities of 793.6 mA h g$^{-1}$ at 800 mA g$^{-1}$ and 712.9 mA h g$^{-1}$ at 1000 mA g$^{-1}$. Although the electrochemical performance for LIBs of those composites has been improved compared to that of pristine NiCo$_2$O$_4$, and the improved performances are still unsatisfied. To further optimize the performance, checkerboard-like NiCo$_2$O$_4$@CNTs have been constructed via multiple-freeze-drying treatment and long-time annealing process. Furthermore, macroporous NiCo$_2$O$_4$/CNTs composite microspheres have been proposed by a multistep process including spray pyrolysis and two-step post-treatment. These strategies can effectively increase the capacity of LIBs but are usually complex and time-consuming, thus unsuitable for the large-scale production. Therefore, it is of great significance to develop an effective strategy for constructing NiCo$_2$O$_4$-based composites electrode with high electrochemical performance via the facile synthetic procedure.

In this work, a simple polyvinyl pyrrolidone (PVP)-assisted method is proposed for fabricating 1D NiCo$_2$O$_4$@CNTs composite as the anode electrode materials for high-performance LIBs. The introduced PVP for modifying pristine CNTs can facilitate the uniform heterogeneous nucleation of nickel/cobalt hydroxide on CNTs via effectively decreasing the interfacial energy between them. The well-designed NiCo$_2$O$_4$@CNTs materials are believed to effectively prevent the agglomeration of active materials and act as an interconnect-conductive network, which benefits diffusion transport for ions and electrons. As a result, the NiCo$_2$O$_4$@CNTs electrode materials exhibit excellent lithium storage performance with high initial discharge capacity (1811.5 mA h g$^{-1}$ at 100 mA g$^{-1}$) and stable cyclic performance (the capacity is 608.1 mA h g$^{-1}$ even at a high current density 2000 mA g$^{-1}$ after 300 cycles). The facile synthetic method developed here is believed general for constructing other nanocomposites with various electrode structures for energy applications.

**RESULTS AND DISCUSSION**

Figure 1 schematically illustrates the synthetic procedure and the resulted architectures of NiCo$_2$O$_4$@CNTs and NiCo$_2$O$_4$@CNTs. First, well-defined NiCo$_2$O$_4$@CNTs precursor was obtained through the heterogeneous nucleation and growth of NiCo-hydroxide on the surface of PVP-modified CNTs under hydrothermal conditions. Subsequently, an annealing treatment in air at 400 °C was performed to transform the NiCo-hydroxide@CNTs precursor into NiCo$_2$O$_4$@CNTs.

The as-prepared NiCo$_2$O$_4$@CNTs precursor was first characterized by X-ray diffraction (XRD) to identify the
crystalline structure. The XRD pattern in Figure S1 matches well with the standard powder diffraction pattern of Ni(OH)$_2$·0.75H$_2$O (JCPDS no. 38-0715). Thus, the obtained NiCo-precursor on the CNTs is probably NiCo-hydroxide, which possesses a similar structure to Ni(OH)$_2$·0.75H$_2$O. Inductively coupled plasma−mass spectrometry analysis confirms that the molar ratio of Ni to Co in the precursor is 1:2. The morphological structure of the NiCo-hydroxide@CNTs precursor was revealed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM image in Figure 2a displays a 1D entire architecture of the precursor that inherits the structure characteristics of the involved 1D CNT template. Without the incorporation of CNT template, the homogeneous nucleation of NiCo-hydroxide only results in the formation of flower-like microspheres (Figure S2). High-magnified SEM image (Figure 2b) reveals that the NiCo-hydroxide@CNTs precursor with a diameter of 90–120 nm has high-density nanosheet arrays on the surface. The well-composited structure is further confirmed by the TEM image in Figure 2c, which exhibits that the CNTs in the core position are firmly encapsulated by uniform nanosheets.

Figure 2. SEM images (a,b) and TEM image (c) of the NiCo-hydroxide@CNTs precursor. The diffusion rates on the surface of pristine CNTs (d−f) and PVP modified CNTs (g−i).

Figure 3. SEM (a,b), TEM (c) and HRTEM (d) images of NiCo$_2$O$_4$@CNTs. Elemental mapping image (e) of an individual NiCo$_2$O$_4$@CNTs.
Significantly, it is found that the modification of pristine CNTs with PVP play a crucial role in directing the uniform heterogeneous nucleation and growth of NiCo-hydroxide on the surface of CNTs. PVP, polymerized from N-vinyl pyrrolidone, possesses abundant oxygen-containing functional groups that can coordinate with Ni and Co ions. Thus, these functional groups can enhance the interaction and decrease the interfacial energy between initially formed Ni, Co-based nucleus, and CNT substrate. Besides, PVP has a high solubility in polar solvents and thus can enhance the compatibility between CNTs and the alcohol solvents. To examine the compatibilities of pristine CNTs and PVP-modified CNTs with the solvent (a mixture of ethanediol and isopropanol) involved in the synthetic procedure, the diffusion rates of the solvent on the surface of these two CNTs were tested and are shown in Figure 2d−i. When a solvent droplet (2 μL) contacts with pristine CNTs, it requires 13 s to completely spread over the surface (Figure 2d−f). In contrast, for PVP-modified CNTs, the droplet spreads over the surface only within 2 s (Figure 2g−i). The confirmed high compatibility between the PVP-modified CNTs and solvent can benefit the contact of the surface of CNTs with Ni and Co-salt precursor, thereby facilitating the process of uniform heterogeneous nucleation and growth. At the same time, PVP-modified CNTs can homogeneously disperse in the solvent and as well facilitate the uniform growth of NiCo-hydroxide. Without the incorporation of PVP, phase separation between NiCo-hydroxide and aggregated CNTs are observed in the SEM image (Figure S3a), further indicating the advantages of PVP for fabricating well-defined NiCo-hydroxide@CNTs. Overall, PVP modification on the surface of CNTs can facilitate the uniform heterogeneous nucleation and growth of NiCo-hydroxide and promote the dispersion of CNTs in the solvent. These advantages integrate together to direct the formation of NiCo-hydroxide@CNTs precursor with a uniform structure.

An annealing treatment process was conducted to transform the NiCo-hydroxide@CNTs precursor to NiCo2O4@CNTs composites. The SEM image in Figure 3a shows that the resulted sample completely retains the 1D morphology of the precursor, indicating the architecture has not been destroyed after the transformation process. Figure 3b reveals that high-density NiCo-hydroxide nanosheets are converted into uniformly distributed nanoparticles on the surface of CNTs. The transformed morphology from nanosheets to nanoparticles is further confirmed by the TEM image in Figure 3c. The as-prepared NiCo2O4@CNTs have a diameter of 60−100 nm. With the NiCo-hydroxide@CNTs precursor prepared in the absent of PVP, separated large NiCo2O4 spheres and aggregated CNTs are obtained (Figure S3b,c). The high-resolution TEM (HRTEM) image (Figure 3d) shows the lattice fringes with interplanar spacings of 0.207 and 0.245 nm, which could be indexed to the (400) and (311) planes of NiCo2O4 phase, respectively. Thus, the NiCo-hydroxide@CNTs precursor has been successfully transformed into NiCo2O4@CNTs. The elemental mapping result of NiCo2O4@CNTs shows the distribution of Ni, Co, O, and C (Figure 4).

Figure 4. XRD pattern (a) and N2 adsorption/desorption isotherm curves (b) of BF–NiCo2O4 and NiCo2O4@CNTs composites. HR XPS spectra of the NiCo2O4@CNTs composites: survey spectrum (c), Ni 2p spectrum (d), Co 2p spectrum (e), and O 1s spectrum (f).
NiCo₂O₄@CNTs (Figure 3e) reveals the uniform distribution of Ni and Co elements throughout the structure. After annealing, the crystalline phases of the resultant samples were analyzed by XRD, as shown in Figure 4a. Well-defined diffraction peaks at 31.1, 36.7, 44.6, 59.1, and 65.0° can be indexed to spinel NiCo₂O₄ (JCPDS no. 02-1074), indicating the high-quality transformation from NiCo-hydroxide to NiCo₂O₄. Both the BF−NiCo₂O₄ and the NiCo₂O₄@CNTs show higher crystallinity than that of NiCo-hydroxide@CNT precursor (Figure S1). No other impurity peaks are observed, which confirms the high purity of NiCo₂O₄ component. The nitrogen adsorption/desorption isotherm curve is provided in Figure 4b, and the specific surface areas and pore volumes are listed in Table S1. The isotherms of BF−NiCo₂O₄ microspheres and NiCo₂O₄@CNTs can be classified as a type IV isotherm in the range of 0.625−0.875 P/P₀, revealing a characteristic mesoporous structure. Notably, the NiCo₂O₄@CNTs display slit-shaped pores which are derived from the typical characteristic of incorporated multi-walled CNTs. The higher specific surface area and the larger pore volume are expected to enhance the diffusion and transport of Li⁺ during the cycle procedure. To confirm the weight ratio of involved CNTs, thermogravimetric analysis (TGA) of the NiCo₂O₄@CNTs was performed from 30 °C up to 900 °C at a temperature rate of 10 °C min⁻¹ (Figure S4). The CNT content in the composite is determined to be 15.36 wt % according to the weight loss of CNTs combustion in an O₂ atmosphere.

The surface composition and chemical valence of the NiCo₂O₄@CNTs hybrid composite were characterized by X-ray photoelectron spectroscopy (XPS). The survey spectrum (Figure 4c) reveals the existence of Ni, Co, O, and C in the composite. By using a Gaussian fitting method, the deconvoluted spectra of Ni 2p, Co 2p, and O 1s are shown in Figure 4d−f. In Figure 4d, the Ni 2p spectrum is fitted with two spin−orbit doublets, characteristics of Ni²⁺ (854 and 871.6 eV) and Ni³⁺ (855.5 and 873 eV) together with two couples of flat satellites (861.4 and 879.5 eV). The Co 2p spectrum is also fitted with two spin−orbit doublets, characteristics of Co²⁺ (779.4 and 794.6 eV) and Co³⁺ (780.9 and 795.9 eV), each
one accompanied with a flat satellite at 785.8 and 803 eV (Figure 4e).\textsuperscript{53} The O 1s spectrum presented in Figure 4f is deconvoluted into three peaks, and the peak at 529.3 eV confirms the metal–oxygen bonds in the lattice. The other two peaks at 530.7 and 533 eV are typically attributed to the existence of defects and surface species such as hydroxyls, chemisorbed oxygen, and physi- and chemisorbed water on the surface.\textsuperscript{54,55} The chemical composition of Ni\textsuperscript{2+}/Ni\textsuperscript{3+} and Co\textsuperscript{2+}/Co\textsuperscript{3+} in the NiCo\textsubscript{2}O\textsubscript{4}@CNT composites confirmed by XPS is consistent with the structure of spinel NiCo\textsubscript{2}O\textsubscript{4}.\textsuperscript{56}

The electrochemical lithium-storage properties of the NiCo\textsubscript{2}O\textsubscript{4}@CNT hybrid as the anode was first evaluated through the cyclic voltammetry (CV) test. Figure 5a gives the CV curves of the first four cycles for the NiCo\textsubscript{2}O\textsubscript{4}@CNTs electrode obtained in the potential range of 0.01–3.0 V at a scan rate of 0.5 mV s\textsuperscript{-1}. The cathodic peak in the first cycle at 1.07 V corresponds to the decompensation of NiCo\textsubscript{2}O\textsubscript{4} to Ni and Co ions (eq 1).\textsuperscript{56}

\[
\text{NiCo}_2\text{O}_4 + 8\text{Li}^+ + 8e^- \rightarrow \text{Ni} + 2\text{Co} + 4\text{Li}_2\text{O} \quad (1)
\]

A sharp peak at around 0.59 V is related to the reduction of Ni/Co ions to Ni and Co metals and the formation of irreversible solid electrolyte interface (SEI) layer and Li\textsubscript{2}O.\textsuperscript{54,57} During the anodic process, the two peaks centered at around 1.49 and 2.25 V are attributed to the conversion of metallic Ni into Ni\textsuperscript{2+} and metallic Co into Co\textsuperscript{3+}, respectively (eqs 2–4).\textsuperscript{51,58}

\[
\text{Ni} + \text{Li}_2\text{O} \rightarrow \text{NiO} + 2\text{Li}^+ + 2e^- \quad (2)
\]

\[
\text{Co} + \text{Li}_2\text{O} \rightarrow \text{CoO} + 2\text{Li}^+ + 2e^- \quad (3)
\]

\[
\text{CoO} + 1/3\text{Li}_2\text{O} \rightarrow 1/3\text{Co}_3\text{O}_4 + 2/3\text{Li}^+ + 2/3e^- \quad (4)
\]

During the subsequent cycles, the main reduction peak shifts to the higher potential at 0.8 V. Notably, the nearly overlapping of the following cycles clearly indicates the desirable electrochemical reversibility of the NiCo\textsubscript{2}O\textsubscript{4}@CNT electrode.

The galvanostatic charge and discharge profiles of the NiCo\textsubscript{2}O\textsubscript{4}@CNTs for the 1st, 10th, 30th, and 50th cycles at a current density of 100 mA g\textsuperscript{-1} are shown in Figure 5b. In the first discharge process, there is an obvious voltage plateau which delivers a discharge capacity of 1806 mA h g\textsuperscript{-1}. With a capacity of 1264.7 mA h g\textsuperscript{-1}, the initial Coulombic efficiency is around 70.0%. According to the present reports, the irrecoverable capacity loss may be related to the formation of SEI film, which is common for most of the anode electrodes.\textsuperscript{51} A capacity of 1135.1 mA h g\textsuperscript{-1} is achieved in the 10th cycle, and the Coulombic efficiency increases to 98.8%. With the increase of the cycled numbers, a capacity of 1155.7 mA h g\textsuperscript{-1} and high Coulombic efficiency of 98.8% is still maintained in the 50th cycle. As a comparison, Figure 5S presents the discharge/charge profiles for the 1st, 10th, 30th, and 50th cycles at a current density of 100 mA g\textsuperscript{-1} of the pristine NiCo\textsubscript{2}O\textsubscript{4} electrode. The pristine NiCo\textsubscript{2}O\textsubscript{4} electrode not only delivers a lower initial capacity of 1067 mA h g\textsuperscript{-1} but also shows a severe capacity fading in the subsequent cycles.

The benefit of the incorporation of CNTs was also verified via the different rate performances between the NiCo\textsubscript{2}O\textsubscript{4}@CNTs and BF–NiCo\textsubscript{2}O\textsubscript{4} electrodes at various current densities (100–2000 mA g\textsuperscript{-1}). As shown in Figure 5c, the NiCo\textsubscript{2}O\textsubscript{4}@CNT electrode delivers a high initial capacity (1283.9 mA h g\textsuperscript{-1} at 100 mA g\textsuperscript{-1}), followed by the capacities of 1099.9, 955.8, 762.6, and 675.6 mA h g\textsuperscript{-1} at the specific current densities of 200, 500, 1000, and 2000 mA g\textsuperscript{-1}, respectively. In contrast, the initial capacity of the BF–NiCo\textsubscript{2}O\textsubscript{4} electrode is only 935.5 mA h g\textsuperscript{-1}. Moreover, because of the sharply dropped capacity with the increased current density, the capacity of BF–NiCo\textsubscript{2}O\textsubscript{4} electrode at 2000 mA g\textsuperscript{-1} is only 9.2% of the capacity of NiCo\textsubscript{2}O\textsubscript{4}@CNTs electrode. When the current density is reversed back to 100 mA g\textsuperscript{-1}, the capacity of the NiCo\textsubscript{2}O\textsubscript{4}@CNT electrode returns to about 996 mA h g\textsuperscript{-1} and then slowly increases because of full penetration of electrolyte. Obviously, the NiCo\textsubscript{2}O\textsubscript{4}@CNT electrode exhibits superior rate performance compared with BF–NiCo\textsubscript{2}O\textsubscript{4} electrode.

To further reveal the advantages of the NiCo\textsubscript{2}O\textsubscript{4}@CNT electrode, Figure 5d compares the cycling behaviors of CNTs, BF–NiCo\textsubscript{2}O\textsubscript{4}, NiCo\textsubscript{2}O\textsubscript{4}/CNT physical mixture (Figure S6), and NiCo\textsubscript{2}O\textsubscript{4}@CNTs at a current density of 100 mA g\textsuperscript{-1}. The capacity of the CNTs sharply drops after the first cycle and then stabilizes at 285.3 mA h g\textsuperscript{-1} after 50 cycles. BF–NiCo\textsubscript{2}O\textsubscript{4} electrode exhibits an obvious capacity fading after 25 cycles, and a capacity of around 398.2 mA h g\textsuperscript{-1} is left after 50 cycles. For the NiCo\textsubscript{2}O\textsubscript{4}/CNT physical mixture electrode, with a first discharge capacity of 850.6 mA h g\textsuperscript{-1}, it shows a rapid capacity decay and only achieves 66.5 mA h g\textsuperscript{-1} at the 50th cycle. Remarkably, the capacities of the NiCo\textsubscript{2}O\textsubscript{4}@CNT electrode for the first and second cycles are, respectively, 1806 and 1232.5 mA h g\textsuperscript{-1}. Starting from the second cycle, the capacity shows very slow fading. A high capacity of 1155.72 mA h g\textsuperscript{-1} is still achieved after 50 cycles, corresponding to ~63.9% of the initial capacity. The Coulombic efficiency rapidly increases to ~100% after the 2nd cycle and keeps highly stable in the following cycles. Compared with BF–NiCo\textsubscript{2}O\textsubscript{4} and NiCo\textsubscript{2}O\textsubscript{4}/CNT physical mixture composites electrode, the superior cycling performance of NiCo\textsubscript{2}O\textsubscript{4}@CNT electrode can be ascribed to the following points. First, the CNTs act as a “core” structure in the NiCo\textsubscript{2}O\textsubscript{4}/CNT nanocomposite with NiCo\textsubscript{2}O\textsubscript{4} “shell” and enhance the performance of the NiCo\textsubscript{2}O\textsubscript{4}/CNT electrode in terms of several aspects: (i) the CNTs with 1D channels serve as high-conductive frameworks that enhance the electron transfer and decrease the polarization of electrodes; (ii) the stable integrated structure formed by CNTs can effectively buffer the volume change of NiCo\textsubscript{2}O\textsubscript{4} and suppress the structural destruction of the composite electrode; and (iii) the CNTs favor the uniform distribution of NiCo\textsubscript{2}O\textsubscript{4} nanoparticles, thus shortening the ion diffusion pathways. In addition, the NiCo\textsubscript{2}O\textsubscript{4} grown on CNTs with a larger specific surface compared with BF–NiCo\textsubscript{2}O\textsubscript{4} can expose more active materials to the electrolyte, which can promote the electrochemical reactions during the charge/discharge process. Significantly, by involving the addition of PVP, the nickel/cobalt (oxo)-hydroxide can in situ grow on CNTs and ensure robust chemical bonds between NiCo\textsubscript{2}O\textsubscript{4} nanoparticles and CNTs after annealing. The interaction allows the composite to well inherit the benefits of CNTs mentioned above. Without the tight interaction, the functions of the CNTs are isolated and the synergetic effect between conductive CNTs and active NiCo\textsubscript{2}O\textsubscript{4} would be absent. As a result, the intimate contact can significantly enhance the functionalization of CNTs in NiCo\textsubscript{2}O\textsubscript{4}@CNTs composite electrode compared with the NiCo\textsubscript{2}O\textsubscript{4}/CNT physical mixture.

With increased current densities (500, 1000, and 2000 mA g\textsuperscript{-1}), the NiCo\textsubscript{2}O\textsubscript{4}@CNT electrode also presents comparable
cycling performance, as shown in Figures S7 and 5e. The discharge capacities stabilize at 739 mA h g$^{-1}$ at 500 mA g$^{-1}$ after 50 cycles and 790.9 mA h g$^{-1}$ at 1000 mA g$^{-1}$ after 100 cycles, respectively (Figure S7). Considering the long cycle life is crucial to the application of LIBs in practice, we further tested the long-term cycling performance of the NiCo$_2$O$_4$@CNT electrode over 300 cycles at a current density of 2000 mA g$^{-1}$ (Figure 5e). It is noteworthy that the NiCo$_2$O$_4$@CNT electrode delivers a high initial discharge capacity of 830.3 mA h g$^{-1}$. With a slow capacity decay, the discharge capacity retains as high as 608.1 mA h g$^{-1}$ after 300 cycles. The corresponding Coulombic efficiency is 94.68% in the first cycle and increases to over 98.8% in the following cycles, confirming the excellent electrochemical reversibility of the electrode even at large current density. Interestingly, there is a trend of gradual increase in the capacities from 80th to 230th cycles, which is probably ascribed to the reversible formation/decomposition of a polymeric gel-like film that can reversibly store lithium. In addition, the high-rate Li$^{+}$ insertion could reactivate the electrode material and probably lead to a structure reconstruction, which is also reasonable for the capacity increase.$^{39}$ Consequently, the capacity reaches a maximum point and begins to decline after long-term cycling. This is a common observation for TMOs based LIBs, and it has been well-documented in previous reports.$^{33,50}$ Based on all the above results, the developed NiCo$_2$O$_4$@CNT composite is among the promising NiCo$_2$O$_4$-based electrodes with superior electrochemical performance (Table S2). The excellent long-term cycling of NiCo$_2$O$_4$@CNT electrode at a high discharge/charge rate (2000 mA g$^{-1}$) ensures tremendous potentials as the anode in applications for LIBs.

The electrochemical impedance spectroscopy (EIS) of the NiCo$_2$O$_4$@CNTs and BF–NiCo$_2$O$_4$ electrodes were carried out to investigate their Li$^{+}$ diffusion kinetics and charge transfer behaviors. Figure 6 shows the Nyquist plots performed at a frequency range from 10 kHz to 0.1 Hz. Both the plots show a single semicircle in the high-to-medium frequency region, which stands for the surface film and the charge-transfer resistance ($R$(sf + ct)) on the electrode–electrolyte interface. The slopes in the low-frequency region stand for the diffusive Warburg impedance ($W_0$) that reflects the solid-state diffusion of Li ions in electrode materials.$^{36,61}$ Clearly, the NiCo$_2$O$_4$@CNT electrode exhibits both smaller $R$(sf + ct) and $W_0$ compared with BF–NiCo$_2$O$_4$, which is indicated by the smaller radius of the semicircle and steeper slope of the NiCo$_2$O$_4$@CNTs electrode. The results of EIS further indicate that the superiority of 1D NiCo$_2$O$_4$@CNT structure discussed above could provide favorable electrical conductivity and accelerate Li ions diffusion.

### CONCLUSIONS

In summary, well-confined NiCo$_2$O$_4$@CNT nanocomposites with robust adhesion between the NiCo$_2$O$_4$ and CNTs have been successfully constructed via a general PVP-assisted hydrothermal method and accompanied by a simple annealing treatment process. Significantly, the introduction of PVP plays an important role in the synthesis of uniform precursor for NiCo$_2$O$_4$@CNTs. PVP could not only make the CNTs well dispersed in solution but also provide abundant oxygen-containing functional groups for combining CNTs with NiCo-hydroxide nanosheets. When the NiCo$_2$O$_4$@CNT composites act as the anode in LIBs, it delivers a reversible capacity of 1141.2 mA h g$^{-1}$ after 50 cycles at a current density of 100 mA g$^{-1}$ (capacity retention of 89.7%). Even up to 2000 mA g$^{-1}$, an excellent initial capacity of 830.3 mA h g$^{-1}$ is achieved, retaining 608.1 mA h g$^{-1}$ after 300 cycles. The improved lithium storage capacity of the NiCo$_2$O$_4$@CNT composites may be attributed to structural stability and interconnected conductive net as well as the high specific surface area. More importantly, the electrode design concept can be facile to grow other TMOs structure on CNT substrates for manufacturing high performance energy storage devices.

### EXPERIMENTAL SECTION

#### Synthesis of Ball-Flower Like NiCo$_2$O$_4$ (BF–NiCo$_2$O$_4$) Microspheres.

NiCo$_2$O$_4$ with a ball-flower like structure was synthesized using a hydrothermal method. First, 0.125 g Ni(CH$_3$COO)$_2$·4H$_2$O and 0.250 g Co(CH$_3$COO)$_2$·4H$_2$O were dissolved in 10 mL ethanol and 47 mL isopropanol. Subsequently, the solution was kept stirring for 30 min at room temperature. Then, the resultant mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 12 h. After cooling to room temperature, brown precipitate was collected by centrifugation and washed with ethanol and deionized (DI) water. After dried at 60 °C for 12 h, the powder was annealed at 400 °C in air for 2 h to obtain BF–NiCo$_2$O$_4$.

#### Synthesis of NiCo$_2$O$_4$@Carbon Nanotubes (NiCo$_2$O$_4$@CNTs).

CNTs (0.01 g) and 0.05 g of PVP were dissolved in 10 mL of ethanediol and 47 mL of isopropanol and sonicated for 12 h. Then, 0.062 g of Ni(CH$_3$COO)$_2$·4H$_2$O and 0.125 g of Co(CH$_3$COO)$_2$·4H$_2$O were added together to the above solution and stirred for 30 min. This solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and kept at 160 °C for 12 h. The autoclave was then allowed to cool to room temperature naturally. The product was collected by centrifugation and washed with DI and ethanol several times and dried at 60 °C for 12 h. The as-prepared product was further treated at 400 °C for 2 h in air, labeled as NiCo$_2$O$_4$@CNTs.

#### Characterization.

The crystalline phases of the as-prepared samples were characterized using an XRD (Rigaku SmartLab 9 kW diffractometer with Cu Kα radiation, $\lambda = 0.15406$ nm). The morphologies and structures of the samples were characterized using an ultrahigh-resolution scanning electron microscope with FEG (SEM, FEI Verios 460L), transmission electron microscope (TEM, Tecnai G2 Spirit TWIN, FEI), and HRTEM with FEG (HRTEM, Talos F200X, FEI). TGA (Netzsch TG 209 F3) was carried out under a flow of air with a temperature ramp of 10 °C min$^{-1}$ from room temperature to 800 °C. The specific surface area and pore size distribution were measured using an adsorption device.
Electrochemical texts, the anode was prepared with active materials (BF–NiCo$_2$O$_4$, NiCo$_2$O$_4$@CNTs or the physical mixture of NiCo$_2$O$_4$ and CNTs), super P and polyvinylidene fluoride (PVDF) at the weight ratio of 70:20:10. The slurry was pasted onto a copper foil substrate and dried in a vacuum oven at 80 °C for 2 h and 120 °C for 12 h in succession. The average mass loading was approximately 1.0 mg cm$^{-2}$. CR2032-type coin cells were assembled using pure lithium metal as the reference electrode. The electrolyte was made by 1.0 M LiPF$_6$ dissolved in a 1:1:1 mixture of ethylene carbonate, ethylene methyl carbonate, and dimethyl carbonate. The coin cells were conducted on a CHI 760D electrochemical workstation. CVs were obtained in the voltage range between 0.01 and 3.0 V at a scan rate of 0.1 mV s$^{-1}$. For EISs, an AC amplitude of 5 mV over the frequency range of 10 kHz to 0.1 Hz was used.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01315.

XRD patterns of samples with different precursors, SEM images of as-prepared BF–NiCo-hydroxide precursor and BF–NiCo$_2$O$_4$, SEM images of NiCo$_2$O$_4$@CNT precursor and SEM and TEM images of NiCo$_2$O$_4$@CNTs without the addition of PVP, TGA curve of the NiCo$_2$O$_4$@CNT composite, charge/discharge profiles of the BF–NiCo$_2$O$_4$ composite electrode at 100 mA g$^{-1}$ current density, SEM image of the NiCo$_2$O$_4$/CNT physical mixture, cycling performance and Coulombic efficiencies of the NiCo$_2$O$_4$@CNT composite, surface area and pore volume of NiCo$_2$O$_4$@CNTs and BF–NiCo$_2$O$_4$ materials, and comparison of the electrochemical performances of typical NiCo$_2$O$_4$ and NiCo$_2$O$_4$-based materials (PDF)

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**Notes**

The authors declare no competing financial interest.

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