Synthesis of Needle-like Nanostructure Composite Electrode of Co$_3$O$_4$/rGO/NF for High-Performance Symmetric Supercapacitor

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Abstract: In this work, a hierarchical electrode structure of cobaltosic oxide (Co$_3$O$_4$) growing on a reduced graphene oxide (rGO)-covered nickel foam (NF) substrate (named Co$_3$O$_4$/rGO/NF) is fabricated by a facile hydrothermal and subsequent annealing process. Thousands of nanoneedle units uniformly arranged on the surface of the rGO sheet stimulate the evident increase in the specific surface area and thus produce more active sites. Because of the special hierarchical structure, the Co$_3$O$_4$/rGO/NF electrode shows a high specific capacitance of 1400 F g$^{-1}$ at 1 A g$^{-1}$ and retains 58% capacitance even when the current density increases to 30 A g$^{-1}$. In addition, a symmetric supercapacitor based on the Co$_3$O$_4$/rGO/NF electrode is assembled, exhibiting high specific capacitance of 311 F g$^{-1}$ at 1 A g$^{-1}$, as well as remarkable power density and energy density (40.67 Wh kg$^{-1}$ at 12 kW kg$^{-1}$). The device also demonstrates a great cycling performance after 10,000 cycles under the current density of 10 A g$^{-1}$, acquiring 89.69% capacitance retention of the initial state. The accessible synthetic method and superior electrochemical performance of the Co$_3$O$_4$/rGO/NF composite electrode implicate its extensive application prospects in terms of new energy storage.

Keywords: Co$_3$O$_4$ nanoneedles; reduced graphene oxide; supercapacitor; symmetric supercapacitor; energy storage

1. Introduction

In recent years, non-renewable mineral energy sources including coal, oil, and natural gas have faced certain dilemmas: The rapid development of the economy results in increasing demands as well as gradually irreversible exhaustion [1,2]. Meanwhile, the environmental pollution caused by burning fossil fuels also hinders sustainable development. Therefore, it is urgently necessary to seek an effective way to resolve the above problems in order to relieve the dependence on fossil fuels and minimize the serious pollution and environmental destruction, which is an inherent reason and powerful motivating force behind the development of new types of energy storage devices [3–6].

Supercapacitors have attracted extensive attention in energy applications due to the advantages of high-power density and their long cycling life [7], which is considered to be ideal for energy storage equipment in many fields, concerning their production and life [2,8]. According to the charge/discharge storage mechanism, supercapacitors can be classified into two categories: The electric double-layer capacitor (EDLC) relies on the charge accumulation at the electrode–electrolyte interface [9], which is associated with the reversible adsorption of ions of the electrolyte onto the electrochemically stable active material electrode under the combined function of coulombic forces, intermolecular forces, and interatomic forces; while the faradaic pseudocapacitor involves rapidly reversible redox reactions and underpotential deposition between the electrolyte and electro-active materials on the electrode surface, producing much higher pseudo-capacitance than the EDLC [10–12]. Generally speaking, carbonaceous materials with high conductivity usually conform to the
EDLC mechanism, which is characterized by an ultrahigh specific surface area, high power density, and good rate performance, but low capacitance values [13,14]. Metal oxides are the most widely used pseudocapacitor material because of the various applicable oxidation states that deliver high specific capacitance and energy density [15]. For example, RuO_2 is considered an electrode material with excellent performance concerning the extremely high specific capacitance and good cycling stability [16,17]. However, the scarcity of resources and exorbitant price have led to restricted applications in large-scale commercial markets; therefore, many researchers have focused on other low-cost transition metal oxides to pursue alternatives to RuO_2.

Co_3O_4 is thought to be the most promising material in supercapacitor applications and has several advantages of ultra-high theoretical specific capacitance (3560 F g^{-1}), stable electrochemical behavior, environmental friendliness, abundant resources, and a convenient synthetic process [18]. Specifically, Co_3O_4 provides an enhanced electrochemical performance because of the rapid and productive redox reaction resulting in high specific capacitance. This typical pseudocapacitive material involves reversible Faradaic redox reactions at the surface and accelerates the charge transfer process, so it can store almost ten times more electrical energy than EDLC materials. Manish et al. prepared Co_3O_4 nanofibers with a specific capacitance of 407 F g^{-1} at a scan rate of 5 mV s^{-1} via the electrospinning technique [19]. Kazemi, S.H. et al. synthesized Co_3O_4 nanoflakes electrode material through a cathodic potential step method and obtained a specific capacitance of 598.9 F g^{-1} at a current density of 6.25 A g^{-1} [20]. However, there are still drawbacks in practical applications of the supercapacitor electrode, including poor conductivity, inadequate cycling stability, and relatively low specific capacitance, which result from the adverse structural collapses caused by the inevitable volume expansion and shrinkage of Co_3O_4 during the charge–discharge process.

Recently, in order to gain efficient supercapacitors with high specific capacitance and excellent cycling performance, many efforts have been made to optimize electrode materials. This is an effective way to synthesize nanocomposites to take advantage of the nanostructure and morphology [21]. Extensive research has been conducted on graphene, as one kind of remarkable carbonaceous material, in energy storage applications because of its good electrical conductivity, high specific surface area, favorable mechanical flexibility, and ultra-thin feature [22,23]. On the other hand, reduced graphene oxide (rGO) is commonly used as a graphene-based material with an accessible and low-cost preparation method, and can be mass-produced and has broad application prospects. Therefore, an efficient method to enhance the cycling stability and achieve high power density and energy density is to develop nanocomposites combining the highly conductive carbonaceous material of rGO and metal oxides with high specific capacitance.

Herein, this paper adopts a cost-effective and convenient strategy to synthesize the nanocomposite by means of hierarchically growing nanometer-sized Co_3O_4 and rGO on a nickel foam substrate. The high-performance composite electrode material (Co_3O_4/rGO/NF) is easily obtained by a simple hydrothermal synthesis method and annealing process. Experimental results show that the low-agglomeration nanocomposite is mainly attributed to the excellent dispersing effect of rGO, which is conducive to avoiding a massive, conglomerated growth of Co_3O_4. The overall preparation process does not use any binder in order to hinder the adverse effects such as electronic transmission blocking, and the depressed specific surface area is avoided, which facilitates the close combination of active materials with the nickel foam or electrolyte. Compared with the Co_3O_4/NF material without the additive rGO, the specific surface area and conductivity of the Co_3O_4/rGO/NF nanocomposite are dramatically increased, resulting in a significant performance boost regarding the specific capacitance and cycling stability.
2. Experiment

2.1. Materials and Reagents

In this experiment, graphite power (Beijing Fine Chemical Co., Ltd., Beijing, China), potassium permanganate (KMnO$_4$, 99.5%, Beijing Fine Chemical Co., Ltd., Beijing, China), sulfuric acid (H$_2$SO$_4$, 98%, Beijing Fine Chemical Co., Ltd., Beijing, China), hydrogen chloride (HCl, Beijing Fine Chemical Co., Ltd., Beijing, China), hydrogen peroxide (H$_2$O$_2$, 30 wt%, Beijing Fine Chemical Co., Ltd., Beijing, China), acetone (CH$_3$COCH$_3$, 99.5%, Beijing Fine Chemical Co., Ltd., Beijing, China), potassium hydroxide (KOH, 99.9%, Beijing Fine Chemical Co., Ltd., Beijing, China), and ethanol (C$_2$H$_5$OH, 99.5%, Beijing Fine Chemical Co., Ltd., Beijing, China), Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, 99.9%, Shanghai Macklin Biochemical Co., Ltd., Shanghai, China), urea (CO(NH$_2$)$_2$, 99.9%, Shanghai Macklin Biochemical Co., Ltd., Shanghai, China), Ni foam (NF, Kunshan Toll Hui Electronics Technology Co., LTD, Kunshan, China.) were analytically pure and could be used without further purification. Deionized water was used in all experimental processes.

2.2. Preparation of Electrode Materials

2.2.1. Preparation of GO and NF

Previous to all the chemical experiments, the graphene oxide (GO) was prepared from the modified Hummers’ method [24], and the details are illustrated in the supporting information pages. Subsequently, GO (100 mg) was dispersed into deionized water (100 mL) by using the ultrasonic treatment for 1.5 h to obtain the homogeneous GO suspension (1 mg mL$^{-1}$). Moreover, an NF sheet (20 mm $\times$ 10 mm $\times$ 1 mm) was constantly cleaned in an ultrasonic bath with 3 mM HCl aqueous solution, acetone, ethanol, and deionized water for 0.5 h, then dried in an oven at 60 $^\circ$C for 18 h.

2.2.2. Preparation of Co$_3$O$_4$/rGO/NF Electrode Material

The process of the electrode materials’ preparation is shown in Figure 1. The pink homogeneous solution was obtained by adding 0.8 mmol (0.233 g) of Co(NO$_3$)$_2$·6H$_2$O and 2.5 mmol (0.15 g) of urea into 7.5 mL of deionized water, followed by mixing in a magnetic stirrer for 30 min. Then, 7.5 mL of the GO suspension was added to the above mixture solution, continually stirring for another 45 min to obtain 15 mL of the mixed solution. Subsequently, a piece of pre-processed NF was immersed into the above mixture, then the entire mixture was transferred into a polytetrafluoroethylene-lined stainless autoclave and placed in an oven at 120 $^\circ$C for 14 h. After the reaction finished, the stainless autoclave was cooled to room temperature, the product was successively washed in an ultrasonic bath with ethanol and deionized water for 15 min, and it was then dried in an oven at 60 $^\circ$C for 4 h. Finally, the Co$_3$O$_4$/rGO/NF electrode material was obtained after the precursor was annealed under the argon atmosphere in a tube furnace at 350 $^\circ$C for 2 h (the apparatus was designed with a temperature changing rate of 5 $^\circ$C min$^{-1}$). For comparison, the samples of Co$_3$O$_4$, Co$_3$O$_4$/rGO, Co$_3$O$_4$/NF, rGO/NF, and pre-rGO/NF were prepared under the same experimental conditions, excluding the additive reactants (specific preparation steps are provided in supporting information pages).
2.3. Structural Characterization

The crystal structures were determined by a Bruker D8 Advance X-ray powder diffractometer (XRD, Berlin, Germany) equipped with Cu Ka radiation (40 kV, 40 mA, \( \lambda = 0.15418 \) nm) over a range of 2\( \theta \) from 10 to 70\( ^{\circ} \). The morphology and microstructure measurements were conducted using scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (TEM, JEM-2010, JEOL, Tokyo, Japan). The surface chemical state was analyzed by X-ray photo electron spectroscopy (XPS, Thermo Scientific Escalab 250Xi, Waltham, MA, USA). Raman spectroscopy (LabRAM HP Evolution, HORIBA, MA, USA) was performed under an excitation wavelength of 514 nm. The nitrogen adsorption and desorption experiment was performed with the Autosorb-IQ NOVA 2000, which is an automatic instrument, while the specific surface area and the pore size distribution were measured by Brunaueur–Emmett–Teller (BET, MICROMERITICS INSTRUMENT CORP ASAP2460, Norcross, GA, USA) and Barrett–Joyner–Halenda (BJH) methods.

2.4. Electrochemical Characterization

In order to evaluate the electrochemical performance of the obtained electrode materials, the prepared electrodes were tested using an electrochemical workstation (CHI 760E, CH Instruments) with a traditional three-electrode system. The prepared materials were used as working electrodes, a platinum electrode was used as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. The testing process in 6 mol L\(^{-1}\) KOH electrolyte solution included cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS). The CV curves were performed in the potential range of \(-0.2\) V to 0.6 V with different scan rates (5~100 mV s\(^{-1}\)). The GCD performance was obtained at a voltage range from \(-0.1\) V to 0.47 V with different electric current densities from 1 A g\(^{-1}\) to 30 A g\(^{-1}\). EIS was obtained with the disturbance amplitude of 5 mV at an open circuit voltage range of 100 kHz to 0.01 kHz. All measurements were conducted at room temperature. On this basis, the specific capacitance of the electrode material was calculated by means of the following expression (1)

\[
C = \frac{I \int V dt}{mV^2}
\]

where \( C \) (F g\(^{-1}\)) represents the specific capacitance of the electrode, \( I \) (A) represents the discharge current, \( \int V dt \) is the integral current area, \( m \) (g) is the mass of the active material, while \( V \) (V) represents the total potential window.

Compared with the traditional three-electrode system, the energy density and power density of the two-electrode system integrated supercapacitor were calculated by the above-
mentioned obtained specific capacitance from (1). The two parameters could be calculated according to the following Equations (2) and (3):

\[
E = \frac{C \times \Delta V^2}{2 \times 3.6} \tag{2}
\]

where \( E \) (Wh kg\(^{-1}\)) is the energy density, \( C \) (F g\(^{-1}\)) is the specific capacitance calculated from the discharge curve, and \( \Delta V \) (V) indicates the potential window.

\[
P = \frac{3600 \times E}{\Delta t} \tag{3}
\]

where \( P \) (W kg\(^{-1}\)) is the power density, \( E \) (Wh kg\(^{-1}\)) represents the energy density, and \( \Delta t \) (s) is the discharge time.

### 3. Result and Discussion

#### 3.1. Morphology and Structural Composition

In order to confirm the crystal structure and phase component of the electrode materials, X-ray diffraction (XRD) characterization was performed, and the result is shown in Figure 2a. Two strong diffraction peaks are the characteristic peaks of the NF substrate in each sample. It can be found that the other diffraction peaks of \( 2\theta = 19^\circ, 31.3^\circ, 36.8^\circ, 44.8^\circ, 55.7^\circ, 59.4^\circ, \) and \( 65.2^\circ \), respectively, correspond to the (111), (220), (311), (400), (422), (511), and (440) planes of the cubic \( \text{Co}_3\text{O}_4 \) phase (PDF#42-1467). Note that the \( \text{Co}_3\text{O}_4 \) phase diffraction peak of \( 2\theta = 44.8^\circ \) is covered by the characteristic peak of the NF. The XRD image of the \( \text{Co}_3\text{O}_4 / \text{rGO} \) sample (Figure S1a) also proves that the composite is successfully obtained. Meanwhile, there is no evident peak of rGO in the XRD patterns of the composites, possibly due to the destroyed regular stacks or low loading of rGO [25].

![Figure 2](https://example.com/figure2.png)

**Figure 2.** (a) Comparison of XRD patterns. Raman spectra of (b) \( \text{Co}_3\text{O}_4 / \text{rGO} / \text{NF} \), \( \text{pre-rGO} / \text{NF} \), and \( \text{Co}_3\text{O}_4 / \text{NF} \) samples and (c) fine spectrum of \( \text{Co}_3\text{O}_4 \). XPS spectra of (d) \( \text{Co} - 2p \), (e) \( \text{O} - 1s \), and (f) \( \text{C} - 1s \) of \( \text{Co}_3\text{O}_4 / \text{rGO} / \text{NF} \) composite.

Raman spectroscopy provides an effective method for the identification of metallic oxide and carbon material, especially for the characterization of graphene. The Raman spectroscopy is measured, and the result is shown in Figure 2b, which clearly indicates
the characteristic peaks of Co$_3$O$_4$, NF, and rGO in the Raman spectra of Co$_3$O$_4$/rGO/NF, Co$_3$O$_4$/NF, and pre-rGO/NF. Meanwhile, the detailed spectrum of the Co$_3$O$_4$ pure sample is shown in Figure 2c. It is obvious that there are five peaks at 184 cm$^{-1}$, 467 cm$^{-1}$, 516 cm$^{-1}$, 615 cm$^{-1}$, and 669 cm$^{-1}$ corresponding to the F$_{2g}$, E$_g$, F$_{2g}$, F$_{2g}$, and A$_{1g}$ modes of Co$_3$O$_4$, respectively [26,27]. In general, the characteristic D-band (the A$_{1g}$ breathing mode) at 1350 cm$^{-1}$ is related to the sp$^3$-carbon or defect structure, while the G-band (the E$_g$ symmetry mode) at 1590 cm$^{-1}$ derives from in-plane vibrations of sp$^2$-carbon atoms, as well as accounting for the integrity of hybrid structures in-plane [28]. Meanwhile, the appearance of the G-band and D-band demonstrates the obtained coating film is composed of well-oriented few-layer graphene [29]. On the basis of the origins of the G-band and D-band, the intensity ratio of I(D)/I(G) is used to quantificationally measure the degree of defect in carbon materials [30]. In Figure 2b, the calculated I(D)/I(G) ratio of the Co$_3$O$_4$/rGO/NF sample is 1.019, while that of the pre-rGO/NF sample is 0.897. It is obvious that the rGO of Co$_3$O$_4$/rGO/NF has a higher I(D)/I(G) ratio than the pre-rGO/NF, which demonstrates the increasing defect concentration in the obtained rGO after the annealing process, resulting in the optimized performance [31].

In addition, XPS analysis affords detailed information in terms of the element composition as well as the types of chemical bonds and states. As shown in Figure S1b, the full XPS wide-scan spectrum of the Co$_3$O$_4$/rGO/NF composite clearly shows the existence of C, O, and Co elements. The high-resolution XPS spectrum of Co 2p (Figure 2d) shows two spin–orbit split lines with the 2p$_{3/2}$ peak at 779.8 eV and the 2p$_{1/2}$ peak at 794.8 eV, respectively, separated by 15.0 eV [32]. The Co 2p$_{3/2}$ contains two satellite peaks at 779.5 eV and 781.2 eV are attributed to Co$^{3+}$ and Co$^{2+}$, respectively [33]. Two satellite peaks at 794.5 eV and 796.2 eV of Co 2p$_{1/2}$ are characteristic peaks of Co$^{3+}$ and Co$^{2+}$, similarly [34]. Note that two satellite peaks (Sat.) belong to the domain of integration Co 2p$_{3/2}$. The peaks at 784.3 eV and 788.9 eV are attributed to oxidized Co, which may be further proof of the interaction between the metal atom and oxygen atom [35,36]. As illustrated in Figure 2e, the XPS spectrum of O 1s contains two peaks identified at 528.8 eV and 530.0 eV. The binding energy of 528.8 eV is considered the typical ionic species of lattice oxygen in Co$_3$O$_4$ [37,38]. The peak located at 530.0 eV is interpreted to be the characteristic signal of the Co–O–C bond, which confirms that Co$_3$O$_4$ is successfully anchored on rGO by effective chemical bonding [39]. The XPS spectrum of C 1s in Figure 2f is separated into three peaks at approximately 284.6 eV, 286.6 eV, and 288.9 eV, corresponding to the bonds of C–C, C–O, and O=C–O, respectively [40]. It can be calculated that the content of oxygen-containing groups is approximately 29.3%, which is far below that of C–C (70.7%), indicating that GO is already reduced to rGO.

SEM and TEM measurements are carried out to analyze the morphology of the prepared materials. Figure 3a shows the silky-smooth surface of the original bare NF sheet, without any loading materials. It is obvious that rGO and Co$_3$O$_4$ are equally loaded on NF by the hydrothermal method (see Figure 3b–c). Figure 3b exhibits a homogeneous coating layer covering the interstice of the original NF, which demonstrates the NF is wrapped with rGO after the hydrothermal treatment. Figure 3c shows that the Co$_3$O$_4$ grown on NF presents in clusters of distributions, with a shape of specially tufted flowers. In Figure 3d, the Co$_3$O$_4$/rGO nanostructure densely and compactly grows onto the NF substrate in the shape of close-knit nanoneedles. By comparison, the partially enlarged view in Figure 3c reveals that the tufted flowers appear as a typical collection resulting in the minification of the specific surface area, while in the Co$_3$O$_4$/rGO/NF sample, every nanoneedle unit shows an evident characteristic of uniform dispersion, which greatly enlarges the specific surface area as well as significantly enhancing the reaction contact. It is also found that there are plentiful open spaces among the nanoneedles, which are beneficial for the remission of volume expansion due to the rapid reversible electrochemical reaction. Therefore, it is clear that the additive rGO plays an important role in dispersing the agminated clusters into plenty of nanoneedles with a fine structure, which is conducive to avoiding the excessive aggregation and adverse volume expansion of Co$_3$O$_4$. In summary, the favorable morphology,
equipped with an abundance of tiny nanoneedles as well as a larger specific surface area, provides more reactive sites due to the stronger contact between the electrolyte ion and exposed active substances; plentiful open spaces among the nanoneedles buffer the volume expansion as well as heightening the permeation of electrolyte ions, establishing a shorter path of ion transmission between the electrode and solution. In addition, the elemental distribution in the Co$_3$O$_4$/rGO/NF composite is also characterized by EDS elemental mapping images (Figure 3e), which demonstrate the uniform and continuous distribution of different elementals (Co, C, and O) in the NF substance. The EDS results corresponding to the spatial distribution of elements are shown in Figure S2, it can be observed that the content of oxygen elements is the highest (43.55%), followed by Co (29.59%) and C (12.75%), demonstrating that the target composite of Co$_3$O$_4$/rGO/NF is successfully synthesized.

Figure 3. SEM images of (a) bare NF, (b) rGO/NF, (c) Co$_3$O$_4$/NF, and (d) Co$_3$O$_4$/rGO/NF (inset: Highly magnified images). (e) EDS elemental mapping images (Co, C, and O), (f) TEM (inset: The nano-needle shape of Co$_3$O$_4$), and (g,h) corresponding HRTEM images and SAED pattern of the Co$_3$O$_4$/rGO/NF composite.

Moreover, the TEM method is carried out to obtain a further analysis of the microstructure and size of the Co$_3$O$_4$/rGO/NF composite. Figure 3f shows the TEM image of the Co$_3$O$_4$/rGO/NF composite, and it can be seen that the Co$_3$O$_4$ nanoneedle arrays deposited on the surface of rGO demonstrate that rGO successfully combines with Co$_3$O$_4$ in the system. Meanwhile, the insert image is further proof that the unit of the sample shows a special nanoneedle shape, which is in accordance with the SEM results. Figure 3g shows the lattice fringes of 0.281 nm, 0.244 nm, 0.165 nm, and 0.205 nm, corresponding to the Co$_3$O$_4$ (220), (331), (422), and (400) crystal planes, respectively, which is consistent with the XRD results. Furthermore, the polycrystalline characteristic of the Co$_3$O$_4$/rGO/NF composite is suggested by means of the correspondingly selected area of the electron diffraction (SAED) pattern (Figure 3h), which demonstrates that the homocentric diffraction rings from inside to outside correspond to the (422), (511), (440), (111), and (311) crystal planes of Co$_3$O$_4$, respectively.

In order to further prove the conclusion, Brunauer–Emmett–Teller (BET) measurements were used to characterize the prepared powder samples with a specific surface
area and pore size distribution. Figure 4a shows the N$_2$ adsorption–desorption isotherms of Co$_3$O$_4$/rGO while Figure 4b is Co$_3$O$_4$, and the illustrations of both pictures show the pore size distribution curves. Both samples present a typical hysteresis loop in the P/P$_0$ range of 0.4–1.0, characterizing the IV sorption behavior, which manifests the presence of the mesoporous structure of the prepared materials. An obvious advantage emerges in the Co$_3$O$_4$/rGO composite, since the specific surface area and average pore size are 74.559 m$^2$ g$^{-1}$ and 9.559 nm, respectively. Compared with the Co$_3$O$_4$/rGO powder, the specific surface area and average pore size of Co$_3$O$_4$ are only 16.815 m$^2$ g$^{-1}$ and 3.808 nm. It can be summarized that the existence of rGO effectively increases the specific surface of the material, thereby giving it countless bonding sites and shortening the distance of charge transfer, which also plays a key role in the dispersing effect for the clustered Co$_3$O$_4$. Meanwhile, the wider pore structure is beneficial to the permeation of the electrolyte solution as well as the speed of electronic and ionic transmission in the electrochemical reaction.

Figure 4. Nitrogen adsorption and desorption isotherm of (a) Co$_3$O$_4$/rGO and (b) Co$_3$O$_4$ with the pore size distribution in the inset.

3.2. Electrochemical Properties

The electrochemical properties of Co$_3$O$_4$/NF and Co$_3$O$_4$/rGO/NF are investigated by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) of testing measurement in the aforementioned three-electrode system with an electrolyte environment of 6 mol L$^{-1}$ KOH. All the electrochemical measurements were performed at room temperature.

Figure 5a shows the CV curves of the Co$_3$O$_4$/rGO/NF composite at different scan rates (from 5 mV s$^{-1}$ to 100 mV s$^{-1}$). It is apparent that several obvious redox peaks are obtained from the cycling characteristic curve of Co$_3$O$_4$ from −0.2 V to 0.6 V, reflecting the mutual transformation between Co$^{2+}$ and Co$^{3+}$ in the redox reaction, explaining the strong pseudocapacitance characteristic of the prepared composite. Furthermore, the shape of CV curves remained almost stable despite the variation in scan rates. The result from the side indicates that the redox coupling was equipped with fine electrochemical reversibility, as well as an excellent electrical conductivity and mass transfer rate. This benefits from its well-graded porous structure, facilitating the infiltration of electrolyte ions with rapid transport. The similar tendency of redox peaks connected to Co$_3$O$_4$ can also be seen in the CV curves of Figure 5b. Urea provides an alkaline environment through the hydrolysis process. The transformation of different cobalt oxidation states due to the corresponding faradaic reactions is shown below:

\[
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow 3\text{CoOOH} + \text{e}^- \\
\text{CoOOH} + \text{OH}^- \leftrightarrow \text{Co}_2\text{O}_3 + \text{H}_2\text{O} + \text{e}^- 
\]
Figure 5. (a,b) CV curves of Co$_3$O$_4$/rGO/NF and Co$_3$O$_4$/NF electrodes under different scan rates. (c,d) GCD curves of Co$_3$O$_4$/rGO/NF and Co$_3$O$_4$/NF electrodes under different current densities. (e) Specific capacitance curves of Co$_3$O$_4$/rGO/NF and Co$_3$O$_4$/NF electrodes under different current densities. (f) Nyquist plots of Co$_3$O$_4$/rGO/NF, Co$_3$O$_4$/NF, and rGO/NF electrodes (inset: High-frequency region).

Generally speaking, the integrated area of the CV curve shows a positive correlation with the capacitance under the same scan rate and voltage window. Comparing Figure 5a with Figure 5b shows that the Co$_3$O$_4$/rGO/NF composite electrode presents a larger integrated area of CV curves than the Co$_3$O$_4$/NF electrode, indicating that the Co$_3$O$_4$/rGO/NF composite, obtained under the same experimental conditions, has a higher capacitance level. Figure 5c,d shows the galvanostatic charge/discharge (GCD) curves at different current densities (from 1 A g$^{-1}$ to 30 A g$^{-1}$) with a voltage window from −0.1 V to 0.47 V. It is obvious that both composites’ GCD curves present evident charge and discharge plateaus corresponding to the redox peaks in the CV curve, which also reflects the pseudocapacitance characteristics of the prepared materials. As shown in Figure S3, the GCD comparison curves of Co$_3$O$_4$/rGO/NF and Co$_3$O$_4$/NF electrodes at a current density of 1 A g$^{-1}$ demonstrate that the Co$_3$O$_4$/rGO/NF electrode equipped with a longer charge–recharge platform results in a higher specific capacitance, indicating the prepared electrode has more advantages in energy storage device field.

Moreover, the calculated specific capacitances of two prepared composites as well as the variation tendency are shown in Figure 5e. The ultra-high specific capacitances of 1400, 1274, 1181, 1120, 1077, 1058, 937, and 812 F g$^{-1}$ are obtained at the current densities of 1, 2, 4, 6, 8, 10, 20, and 30 A g$^{-1}$, respectively, for the Co$_3$O$_4$/rGO/NF composite, while the calculated Co$_3$O$_4$/NF values are 899, 724, 623, 590, 563, 532, 397, and 321 F g$^{-1}$ at 1, 2, 4, 6, 8, 10, 20, and 30 A g$^{-1}$, respectively. Meanwhile, we note that the Co$_3$O$_4$/rGO/NF electrode exhibits a better rate performance, and despite the 30-fold increase in current densities, 58% of specific capacitance is still maintained, which is superior to the Co$_3$O$_4$/NF electrode with 36%. Moreover, the specific capacitances of the two prepared electrodes gradually decrease with the increase in current density, which can be explained by the fact that the fast-moving electrolyte ions equipped with a rapid in-and-out rate find it difficult to enter the interior of the materials under the high current density, generating specific capacitance stemming from the reaction between electrolyte ions and the active
substance on the surface of the material. The excellent electrochemical performance can be attributed to the special composite structure for the following reasons: (1) The abundant defect structure of rGO obtained by the annealing process provides countless bonding sites as well as greatly accelerating the electron transfer rate of the electrode regarding the redox reaction; (2) the rGO contributes to spreading out the Co$_3$O$_4$ particles uniformly thanks to its large specific surface area and good electrical conductivity; (3) the meticulous, nanoneedles of the closely spaced coating obtained provide plentiful open spaces, making for a shorter migration path of the electrolyte ions as well as the remission of volume expansion during the charging and discharging processes; (4) the active substances grow directly on the NF conductive substrate without any additive binder, which betters the spatial adhesion connected to the current collector, as well as guaranteeing the efficient utilization of pseudocapacitance; (5) the NF substrate is a type of well-conducting porous material equipped with a three-dimensional structure, which creates favorable conditions for the full infiltration of active substances into the electrolyte. In conclusion, the fast electron transport ability and countless electrochemical active sites are obtained by the direct growth of Co$_3$O$_4$ on NF and the tightly enclosed structure of the rGO coating, which will help to guarantee the efficient, conductive faraday reactions so as to enhance the electrochemical performance of the electrode markedly.

Moreover, EIS testing is carried out to further evaluate the electrical conductivity and charge transport performance of the prepared electrode materials. Figure 5f shows the Nyquist plots of Co$_3$O$_4$/rGO/NF, Co$_3$O$_4$/NF, and rGO/NF, ranging from 100 kHz to 0.01 kHz, which consists of two parts: a tiny semicircle in the high-frequency region and an approximately straight line in the low-frequency region. The intercept of the X-real axis (Z’$''$) indicates the internal resistance (R$_s$) of the material, mainly including the electrolyte impedance, the intrinsic impedance of the material, and the juncture impedance of the electrode material/current collector interface. The size of the semicircle in the high-frequency region of curves, on behalf of the charge-transferring impedance (R$_{ct}$), mainly stems from the redox reaction and double layer capacitance on the surface of materials. Meanwhile, the slope of the line in the low-frequency region is closely related to the diffusion impedance (Warburg impedance) from the electrolyte ions, whereby a greater slope represents a shorter diffusion distance for electrolyte ions, which contributes to less diffusion resistance. Figure 5f shows there is no obvious semicircle in the composite, verifying its small charge-transferring distance for electrolyte ions, which contributes to less diffusion resistance. Figure 5f shows there is no obvious semicircle in the composite, verifying its small charge-transferring impedance, which indicates that the composite is equipped with rapid charge transfer capacitance and tight contact between the electrochemically active material and the current collector. In the low-frequency region, the Co$_3$O$_4$/rGO/NF composite shows a greater vertical slope than the Co$_3$O$_4$/NF sample, which illustrates the electrolyte exhibits better permeability for the Co$_3$O$_4$/rGO/NF electrode material, that is to say, less diffusional resistance of the electrolyte exists in the Co$_3$O$_4$/rGO/NF system. As a result, the Co$_3$O$_4$/rGO/NF composite has more advantages as the electrode material of the supercapacitor due to the additive rGO.

A type of symmetric supercapacitor device has been assembled to confirm the potential application of the Co$_3$O$_4$/rGO/NF composite. A piece of filter paper was used as a separator (adding filter paper can protect the supercapacitor from an electrical short-circuit), and the electrochemical performance testing processes are carried out in 6 mol L$^{-1}$ KOH electrolyte.

The CV curves of the symmetric supercapacitor at different scan rates (5~100 mV s$^{-1}$) are illustrated in Figure 6a. In order to illustrate the charge storage mechanism for both electrodes, a kinetic analysis is performed by considering the CV curves (Figure S4). The b value is calculated as 0.84 via the formula of $i = a \times \nu^b$, which is confirmed as pseudocapacitance. Unlike the aforementioned three-electrode system, the approximate rectangle of the CV curves is without obvious oxidation and deoxidization peaks, which is observed in previous research [41,42]. Meanwhile, there is no severe deformation in the CV curves of various scan rates, which demonstrates the ideal capacitive performance and good rate stability of the supercapacitor device. GCD curves at different current densities are further shown in Figure 6b, and the specific capacitances are calculated as 311, 292, 256,
241, 232, 218, and 203 F g\(^{-1}\) at 1, 2, 4, 6, 8, 10, and 20 A g\(^{-1}\), respectively. Figure 6c shows the multiplier performance curves obtained by Figure 6b, which further proves the good capacitance retention of the device. The above charge-discharge curves present a similar isosceles triangle, indicating the device is equipped with ideal capacitance characteristics. Moreover, CV and GCD testing of the symmetric supercapacitor by means of changing the voltage range from 0 V to 0.6 V (Figure S5) shows the shape of CV and GCD curves still remain almost unchanged, indicating that the Co\(_3\)O\(_4\)/rGO/NF supercapacitor can operate with stable performance under different working voltages, ranging from 0 V to 0.6 V.

**Figure 6.** (a) CV curves of the device at different scan rates ranging from 5 to 100 mV s\(^{-1}\). (b) GCD curves of the device at different current densities ranging from 1 to 20 A g\(^{-1}\). (c) Specific capacitances of the device at different current densities. (d) Cycling performance at a current density of 10 A g\(^{-1}\) for 10,000 cycles. (e) Nyquist plot of the device before and after cycles (inset is the plot in the high-frequency region).

In addition, in the working voltage range of −0.6 V to 0.6 V, the cycling performance curve of the symmetric supercapacitor at a current density of 10 A g\(^{-1}\) is shown in Figure 6d, where the capacitance retention rate reaches approximately 89.69% of the initial value after 10,000 cycles, which distinctly exhibits the good electrochemical cycling stability of the device. The surface morphology of the cycled Co\(_3\)O\(_4\)/rGO/NF electrode is also observed in SEM images (Figure S6), and it can be seen that nanoneedles still maintain an interlaced distribution form, with slight distortion. The good cycling stability is mainly due to the flexibility, high mechanical strength, and excellent electrical conductivity of the graphene sheet layer during the charge-discharge process, which diminishes the shedding and deformation of the Co\(_3\)O\(_4\) nanostructure. Figure 6e shows the contrastive Nyquist plots of the symmetric supercapacitor device before and after the cycling performance testing, and it can be seen that the electrochemical impedance of the device still maintains a relatively low-value level after 10,000 cycles. In conclusion, the assembled symmetric supercapacitor device possesses ideal electrochemical performance, which has research value and potential for practical applications.

According to the calculation of the measured data, the maximum energy density of the prepared device is up to 62.2 Wh kg\(^{-1}\) at the power density of 599.84 W kg\(^{-1}\), and the energy density is 40.67 Wh kg\(^{-1}\) at the high power density of 12 kW kg\(^{-1}\), indicating that the symmetric supercapacitor has the advantages of good charge storage capacitance
as well as high energy density and power density, which benefit from the rich porous structure and higher specific surface area of the prepared Co$_3$O$_4$/rGO/NF composite electrode. The remarkable performance of the nano-needle Co$_3$O$_4$/rGO/NF symmetric supercapacitor in capacitance and cycling stability reveals its possibility and feasibility of application potential.

4. Conclusions

In conclusion, a type of nano-needle Co$_3$O$_4$/rGO/NF composite electrode material is successfully synthesized by means of a facile hydrothermal method with a simple annealing process without using any binder. The remarkable conductivity and electrochemical reversibility of the hybrid composite are the results of the synergistic effect between Co$_3$O$_4$ and the graphene material, which contributes to the specific capacitance of the Co$_3$O$_4$/rGO/NF electrode, achieving 1400 F g$^{-1}$ at 1 A g$^{-1}$ in 6 mol L$^{-1}$ KOH solution. A symmetric supercapacitor device is fabricated by Co$_3$O$_4$/rGO/NF composite electrodes and also exhibits a high specific capacitance of 311 F g$^{-1}$ at 1 A g$^{-1}$, even at 20 A g$^{-1}$ and still up to 203 F g$^{-1}$. The device presents an excellent energy density of 62.2 Wh kg$^{-1}$ at a power density of 599.84 W kg$^{-1}$ and retained 40.67 Wh kg$^{-1}$ at a high power density of 12 kW kg$^{-1}$. In addition, at the current density of 10 A g$^{-1}$, the symmetric supercapacitor also delivers an excellent long cycle life along with capacitance retention of 89.69% after 10,000 cycles. This supercapacitor device, with its excellent performance, paves the way for promising practical applications in the energy storage devices field.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst12050664/s1, Figure S1: (a) XRD pattern of the Co$_3$O$_4$/rGO composite; (b) full XPS wide-scan spectrum of the Co$_3$O$_4$/rGO/NF composite; Figure S2: EDS elemental mapping images of needle-like Co$_3$O$_4$/rGO/NF (the Ni signal is from NF substrate); Figure S3: Comparison GCD curves of Co$_3$O$_4$/rGO/NF and Co$_3$O$_4$/NF electrodes at 1 A g$^{-1}$. Figure S4: (a) CV curves of the device at different voltage windows at the scanning rate of 75 mV s$^{-1}$ and (b) GCD curves of the device at different voltage windows at 6 A g$^{-1}$; Figure S5: Top-view SEM image of Co$_3$O$_4$/rGO/NF after the 10,000 cycles.

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