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Hexadecyl trimethyl ammonium bromide assisted growth of NiCo_2O_4 @reduced graphene oxide/nickel foam nanoneedle arrays with enhanced performance for supercapacitor electrodes†

Tingting Liu,^{*a} Shuai Zhou,^b Xuehan Yu,^b Chao Mao,^b Yujie Wei,^b Xinyong Yu,^b Lei Chen,^a Xin Zhao,^b Guoxing Tian^b and Ling Chen^{id} ^{*bc}

NiCo_2O_4 @reduced graphene oxide (rGO)/nickel foam (NF) composites were prepared via a hydrothermal method followed by annealing assisted by hexadecyl trimethyl ammonium bromide (CTAB). NiCo_2O_4 @rGO/NF nanoneedle arrays grew directly on Ni foam (NF) without using a binder. The effect of graphene oxide (GO) concentration on the electrochemical properties of the composite was studied. When the GO concentration was 5 mg L^{-1} , the as-prepared NiCo_2O_4 @rGO/NF reaches the highest specific capacitance of 1644 F g^{-1} at a current density of 1 A g^{-1} . Even at 15 A g^{-1} , the specific capacitance is still 1167 F g^{-1} and the capacitance retention rate is 89% after 10 000 cycles at 10 A g^{-1} . Furthermore, a NiCo_2O_4 @rGO/NF/graphene hydrogel (GH) asymmetric supercapacitor cell (ASC) device was assembled and exhibits a high specific capacitance of 84.13 F g^{-1} at 1 A g^{-1} and excellent cycle stability (113% capacitance retention) after 10 000 charge/discharge cycles at 10 A g^{-1} . This provides potential for application in the field of supercapacitors due to the outstanding specific capacitance, rate performance and cycle stability of NiCo_2O_4 @rGO/NF.

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1. Introduction

With the aggravation of global warming and the exhaustion of fossil energy, the development and application of new energy materials are extremely urgent. On the one hand, new energy industries such as solar energy, wind energy and tidal power have promising prospects, but these energy sources have certain limitations in terms of time or space. In order to completely replace the original thermal power generation, matching energy storage systems are needed to achieve the continuous and stable output of electric energy. On the other hand, new energy vehicles represented by electric vehicles will replace traditional fuel vehicles to become the mainstream of transportation in the future, which will be a revolution in the world automobile industry and the inevitable result of low-carbon economic development. The key to overcome fuel vehicles is to develop

efficient energy storage devices with high energy density and power density, long cycle life and good safety. In addition, with the continuous progress of technology and the acceleration of informatization, there is an increasingly urgent demand for high-performance energy storage components in the military, industry, communication and other fields.

As efficient, environmentally friendly and new-type energy storage elements, supercapacitors have many advantages of both traditional capacitors and batteries, such as large capacitance, high energy density and power density, wide operating temperature range, long cycle life,^{1,2} etc. They have attracted great attention in the world and become one of the important advanced technologies in the energy field. Electrode materials are the main component of supercapacitors and the key index to determine their performance. The research on the preparation and performance of electrode materials has always been the focus of the field of supercapacitors. Double-layer capacitor electrode materials represented by carbon materials^{3,4} and pseudocapacitance electrode materials represented by transition metal oxides/hydroxides⁵⁻⁷ and conductive polymers^{8,9} have their own advantages, and considerable progress has been made in related researches. Among numerous transition metal oxides, NiCo_2O_4 is a kind of mixed metal oxide with low price and abundant resource.^{10,11} NiCo_2O_4 is spinel structure, which can be considered to be formed by replacing Co with Ni in Co_3O_4 . There are $\text{Co}^{3+}/\text{Co}^{4+}$, $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ redox

^aNortheast Petroleum University Qinhuangdao, Qinhuangdao, Hebei 066004, China. E-mail: 2008little@163.com; Fax: +86 335 8065113; Tel: +86 335 8065113

^bHebei Key Laboratory of Applied Chemistry, College of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao, Hebei 066004, China. E-mail: hhchen@ysu.edu.cn; Fax: +86 335 8061569; Tel: +86 335 8061569

^cHebei Key Laboratory of Heavy Metal Deep-Remediation in Water and Resource Reuse, College of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao, Hebei 066004, China

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reaction pairs in the charge–discharge process. Therefore, NiCo_2O_4 has higher electrochemical activity than pure nickel or cobalt oxides, and its electronic conductivity (10^{-1} to 10^2 S cm^{-1}) is better than Co_3O_4 and NiO .^{12,13} Based on this, NiCo_2O_4 has become the research hotspot of electrode materials for supercapacitors in recent years. However, its poor cycle stability and rate performance limit its application in practice. In order to improve the electrochemical properties of NiCo_2O_4 materials, a lot of researches have been carried out.

The construction of special complex nanostructures is an effective strategy. Special nanostructures have significant effects on the properties of materials. Numerous NiCo_2O_4 materials with various morphologies have been designed and synthesized, including nanosheets,^{14,15} nanowires,^{16,17} nanorods,^{11,18} microspheres,^{19,20} hexahedrons,²¹ *etc.* These morphologies have their own advantages, but also have their limitations. One-dimensional nanostructures such as nanowires are beneficial to the assembly of nanodevices, but their own specific surface area is small and they cannot provide enough active sites in the reaction process. Two-dimensional nanostructures such as nanosheets have a large specific surface area, which can provide more electron transport channels and make full use of the active materials. However, nanosheets tend to form layered stacks, and their stability will decline after several charge–discharge cycles. Compared with simple structures, complex stereoscopic cross structures, such as core–shell structure²² and yolk–shell structure²³ have more advantages in preventing internal particle agglomeration, providing more active sites for electrochemical reactions and effectively shortening ion diffusion paths. At the same time, the space between shells can buffer the residual pressure caused by volume expansion/contraction during the repeated Faraday reaction.

Besides, NiCo_2O_4 compounds with different materials can combine the advantages of various materials and produce synergistic effect, which is expected to obtain more outstanding electrochemical performance. Most of the researches were focused on loading transition metal oxides such as MnO_2 ,²⁴ Ni(OH)_2 (ref. 13) on the surface of NiCo_2O_4 , or

loading NiCo_2O_4 on porous materials with large surface area and high conductivity, such as nickel foam (NF)²⁵ and carbon materials,²⁶ *etc.* Among them, graphene as an infinitely scalable two-dimensional crystal material, which has a large specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), good electronic conductivity and chemical stability,²⁷ has been widely used in the preparation of composite electrode materials for supercapacitors since it was successfully isolated from graphite by Geim group in 2004.²⁸ In addition, one-dimensional carbon nanotubes (CNTs) are also commonly used in the preparation of composite materials.²⁹

By integrating the above two approaches, the special composite microstructure constructed by integrating several materials with different structures is considered to be a more effective method to obtain excellent electrode materials for supercapacitors due to its good synergistic effect. Zhang *et al.*³⁰ synthesized reduced graphene oxide (rGO)/ NiCo_2O_4 composites, in which the rGO was coated on the NiCo_2O_4 nanowires with no aggregation. The unique heterostructured rGO/ NiCo_2O_4 nanostructures exhibit high specific capacitance, excellent cycling stability and good rate capability in the application for supercapacitors, resulting from the interconnected porous frameworks and the strong interface polarization. Yang *et al.*³¹ reported mesopores NiCo_2O_4 nano-needles directly grown on nickel foam for high-performance supercapacitors by one-step hydrothermal method. The unique structure of mesopores increased the contact efficiency between the active materials and the electrolyte, which made the electrolyte easily penetrate the electrode and achieved a high capacitance response to have effective storage application. Wei *et al.*³² developed a green pre-adjusted pH value aq. phase coprecipitation strategy assisted by citric acid, followed proper annealing at different temperature for the first time to synthesize novel honeycombed-like composites $\text{NiCo}_2\text{O}_4/\text{rGO}$. $\text{NiCo}_2\text{O}_4/\text{rGO}$ -250 (at 250°C) shows considerable specific capacitance, high rate performance and good cycling stability for supercapacitor, which could be attributed to the highly-ordered 3D honeycombed-like nano-sheet array leading to high specific surface area and numerous open macroporous network giving sufficient electroactive sites.

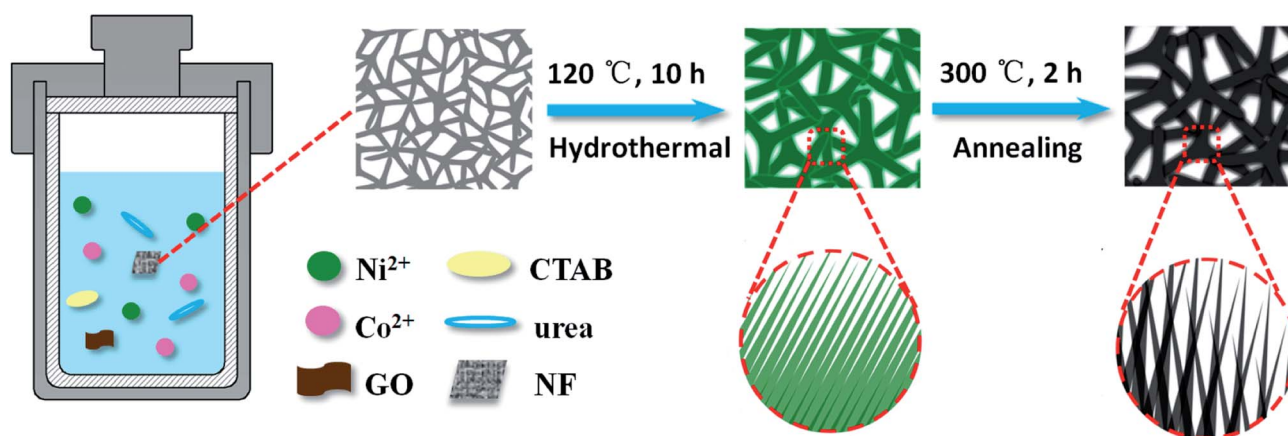


Fig. 1 Schematic synthesis procedure of $\text{NiCo}_2\text{O}_4/\text{rGO}/\text{NF}$.



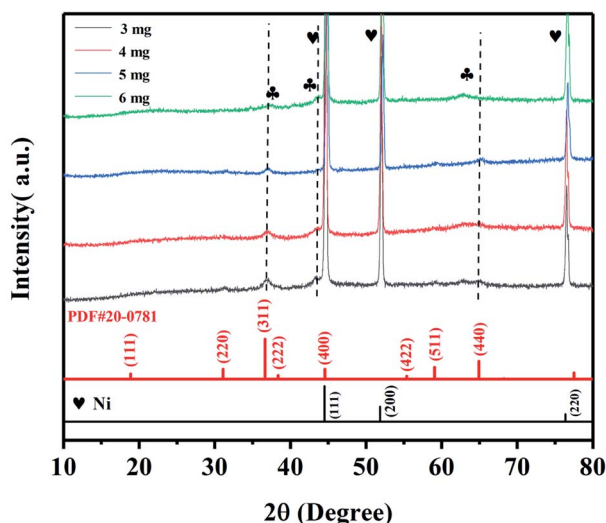


Fig. 2 XRD patterns of $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ with different concentration of GO.

In brief, extensive researches revolved around the synthesis technology, morphology control, structural design and electrochemical performance improvement of NiCo_2O_4 composites.

In this work, a simple strategy was used to prepare $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ composites assisted by hexadecyl trimethyl ammonium bromide (CTAB) *via* hydrothermal method followed annealing. The prepared $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ was applied to supercapacitors and the electrochemical performance was evaluated. In the process, the effect of graphene oxide (GO) concentration on the electrochemical properties of the composite was also investigated. It is believable that the synthetic strategy, the morphological control and the application of $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ electrode materials with enhanced performance in the field of supercapacitor could provide reference for researchers.

2. Experimental

2.1. Preparation of $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ and $\text{NiCo}_2\text{O}_4/\text{NF}$

1 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 4.5 mmol of urea were added into 20 mL of deionized water and stirred. Then 0.5 mmol of CTAB was added into the above solution with continuous stirring, and dispersed under ultrasonication for 30 min. GO was prepared by the modified Hummers' method.³³ A certain mass of GO was weighed and added into 10 mL of deionized water to form uniform dispersion under ultrasonication with a range of concentrations (3, 4,

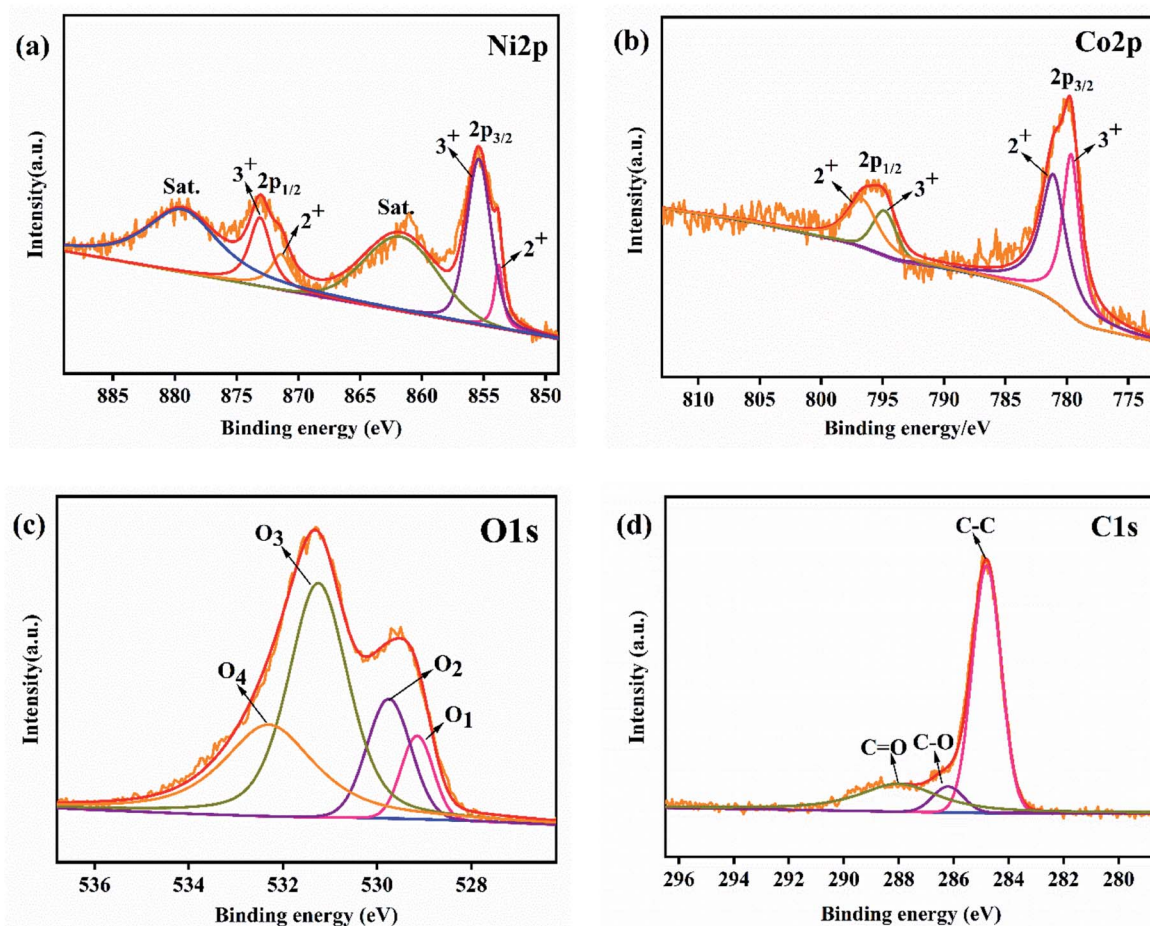


Fig. 3 XPS spectra of (a) Ni 2p, (b) Co 2p, (c) O 1s and (d) C 1s of the $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ (GO 5 mg L^{-1}).



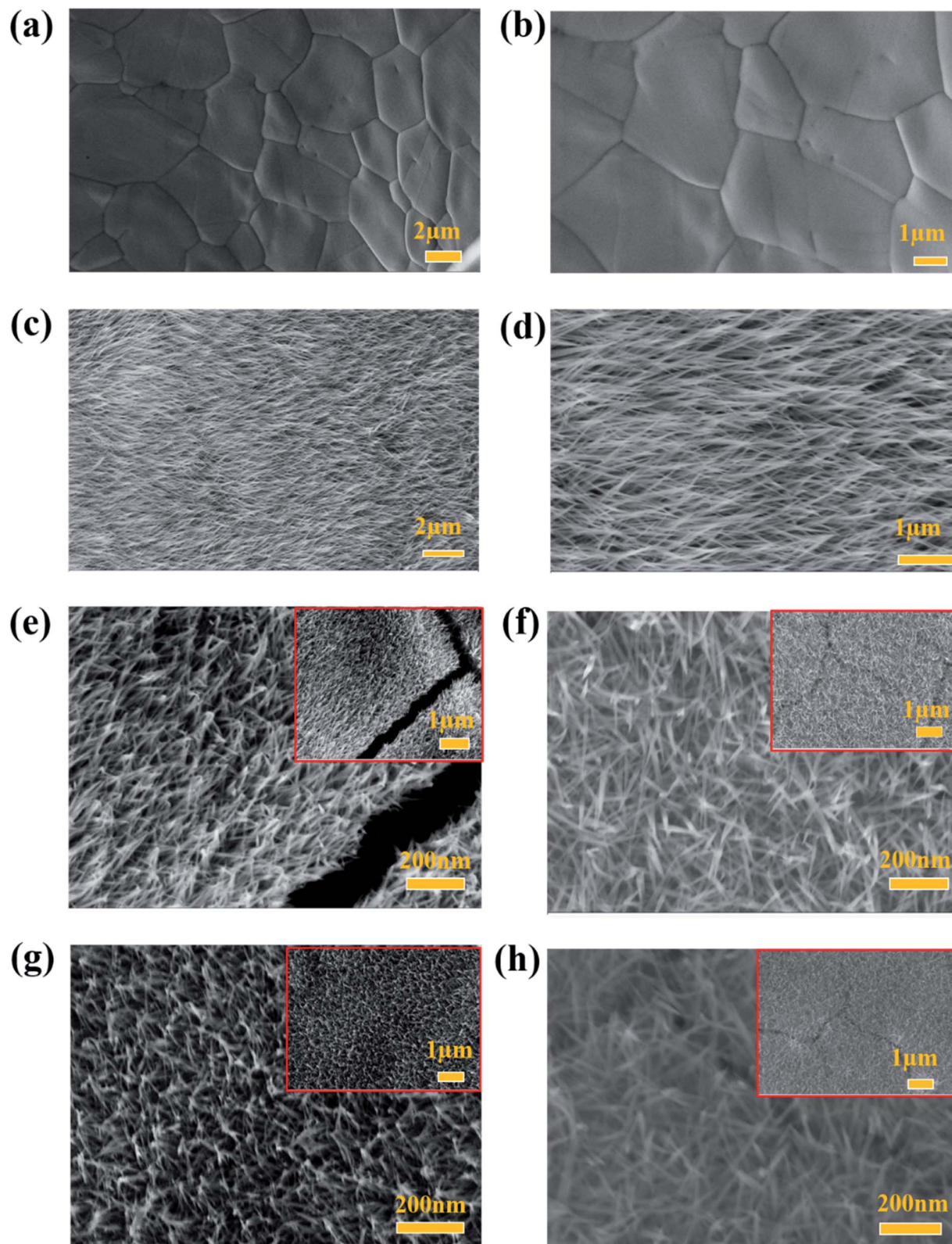


Fig. 4 SEM images of (a and b) bare Ni foam (c and d) $\text{NiCo}_2\text{O}_4/\text{NF}$, (e) $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ ($\text{GO } 3 \text{ mg L}^{-1}$), (f) $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ ($\text{GO } 4 \text{ mg L}^{-1}$), (g) $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ ($\text{GO } 5 \text{ mg L}^{-1}$) and (h) $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ ($\text{GO } 6 \text{ mg L}^{-1}$).



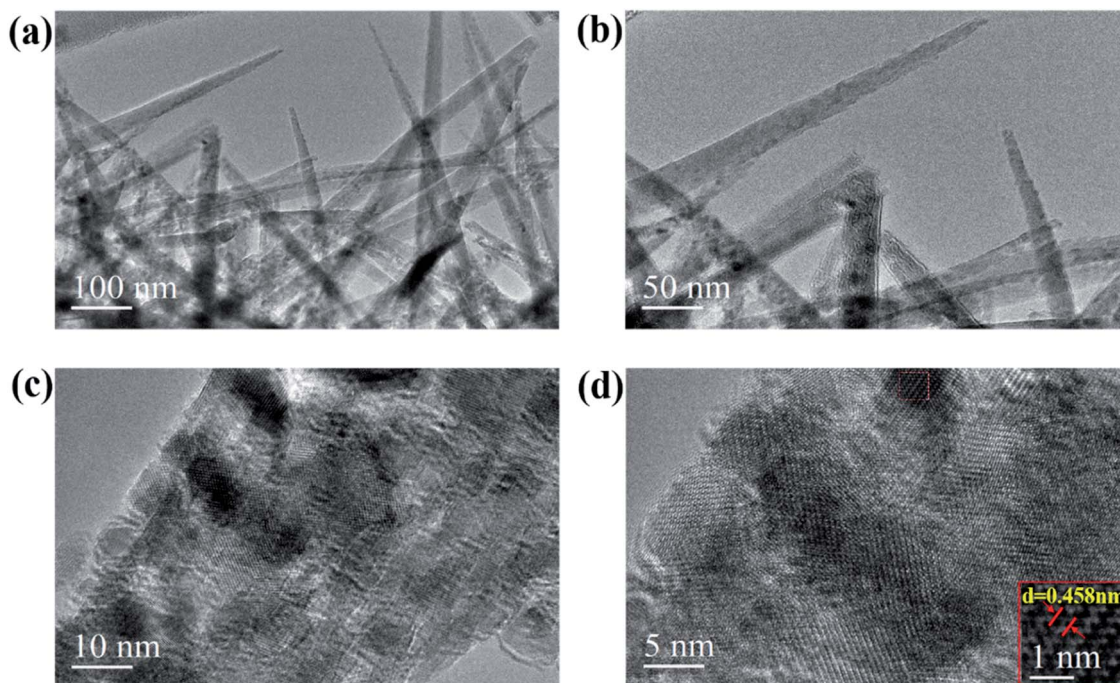


Fig. 5 (a, b) TEM and (c, d) HRTEM images of $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ ($\text{GO } 5 \text{ mg L}^{-1}$).

5 and 6 mg mL^{-1}) for later use. All the chemical reagents are of analytical grade.

The above two solutions were mixed and stirred for 40 min, then transferred into a Teflon lined stainless steel autoclave, in which a piece of nickel foam (NF) ($1 \text{ cm} \times 1 \text{ cm}$) was immersed, then reacted at 120°C for 10 h. After cooling to room temperature, the nickel foam was rinsed with deionized water and ethanol. The product was dried at 60°C for 12 h. Finally, $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ composites were obtained after annealing at 300°C for 2 h. Simultaneously, $\text{NiCo}_2\text{O}_4/\text{NF}$ was synthesized by

the same way, but in absence of rGO for comparison. The schematic synthesis procedure of the $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ composites is illustrated in Fig. 1. In brief, firstly, $\text{NiCo}_2(\text{OH})_6$ was formed in the hydrothermal reaction,³⁴ and CTAB played a role of controlling the morphology of the products during the reaction.³⁵ Then, NiCo_2O_4 was acquired after further heat treatment.

2.2. Characterization

The phase structures of the as-prepared materials were performed using the powder X-ray diffraction (XRD, D-max-2500/

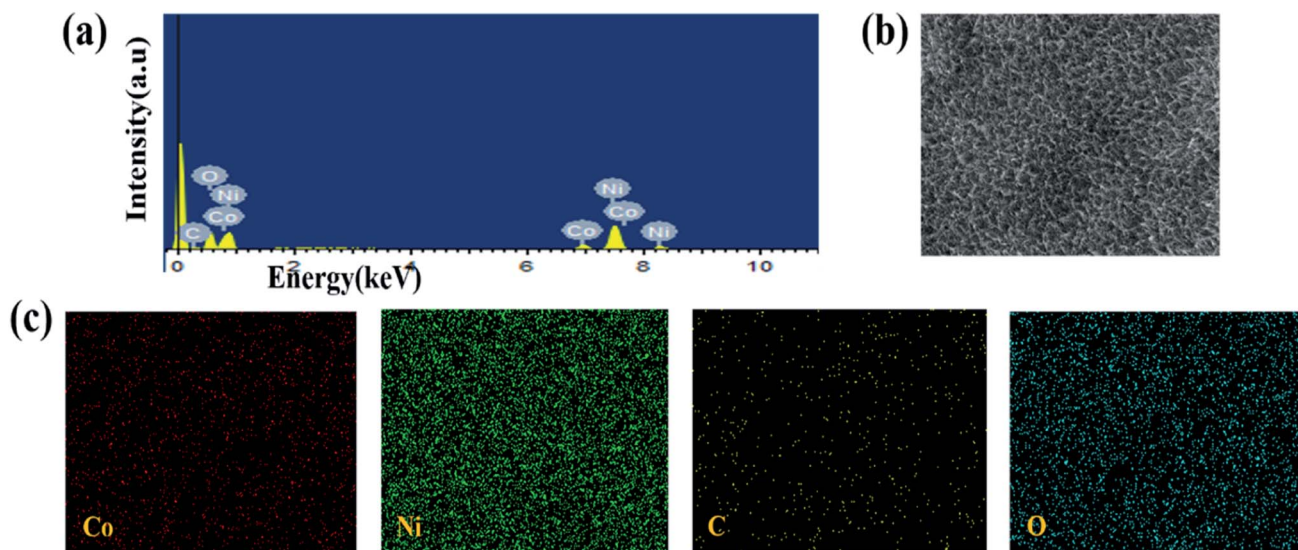


Fig. 6 (a) SEM energy dispersive spectroscopy, (b) SEM and (c) SEM element mapping of $\text{NiCo}_2\text{O}_4@\text{rGO}/\text{NF}$ ($\text{GO } 5 \text{ mg L}^{-1}$).

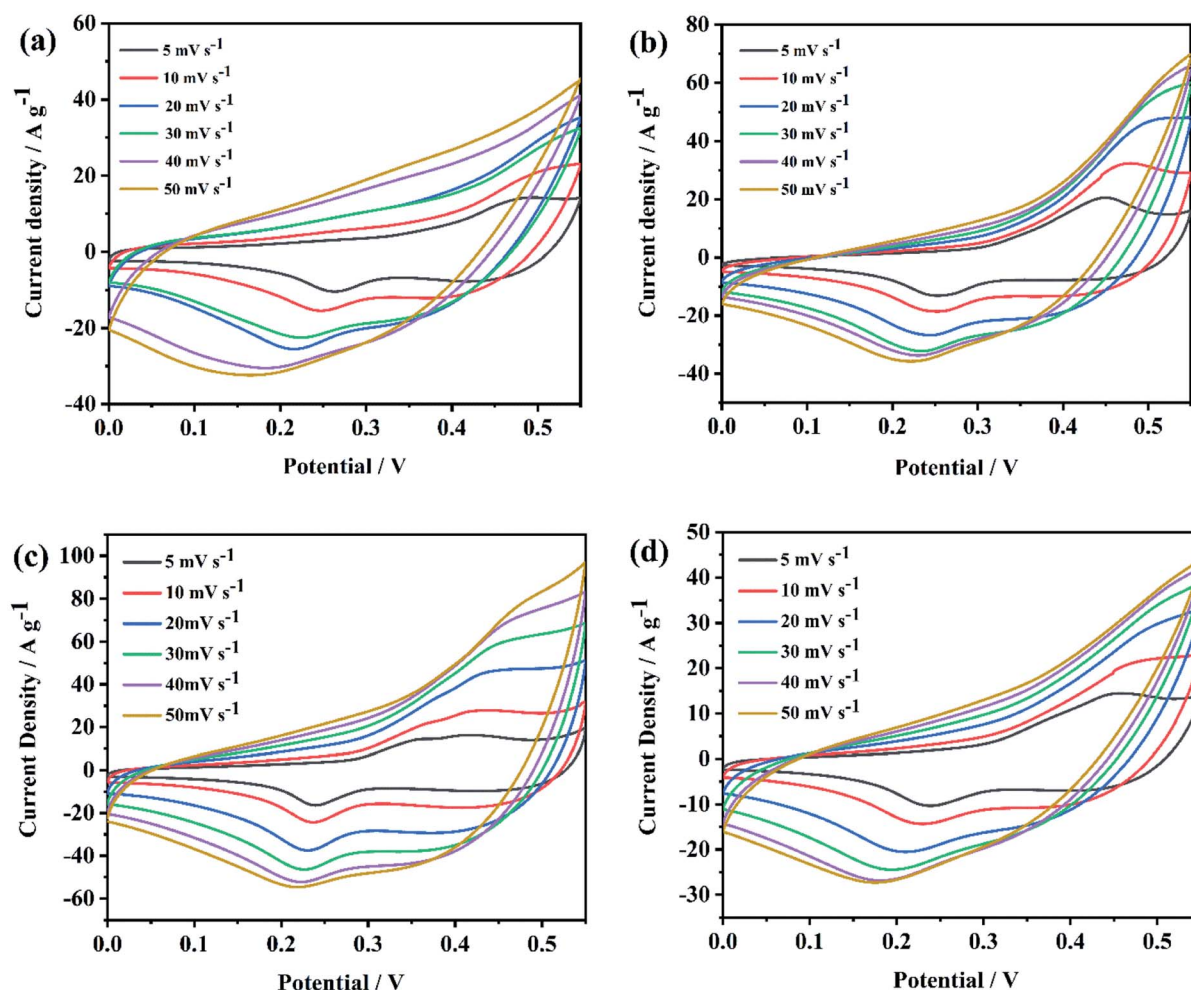


Fig. 7 CV curves of NiCo₂O₄@rGO/NF with different concentration of GO at various scan rates: (a) NiCo₂O₄@rGO/NF (GO 3 mg L⁻¹), (b) NiCo₂O₄@rGO/NF (GO 4 mg L⁻¹), (c) NiCo₂O₄@rGO/NF (GO 5 mg L⁻¹) and (d) NiCo₂O₄@rGO/NF (GO 6 mg L⁻¹).

PC, Rigaku) with Cu K α radiation ($\lambda = 0.15406$ nm) over a range $2\theta = 10^\circ$ – 80° . The morphologies were characterized by scanning electron microscopy (SEM, KYKY-2800B) and transmission electron microscopy (TEM, Hitachi HT-7700). The elemental analysis was detected by X-ray photoelectron spectroscopy (XPS, Thermal ESCALAB 250).

2.3. Electrochemical measurements

The nickel foam loaded with active material was pressed under a pressure of 10 MPa, and then soaked in 6 M KOH solution for 24 h. The electrochemical performance was tested in a three-electrode system with 6 M KOH aqueous as the electrolyte. The as-prepared active material was used as the working electrode, platinum plate (1 cm \times 1 cm) electrode as the counter electrode and Hg/HgO electrode as the reference electrode. Galvanostatic charge–discharge (GCD) tests were performed *via* a charge–discharge instrument (Neware CT-3008, Shenzhen, China) with a potential window of 0–0.45 V. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on a CHI660E electrochemical workstation

(Chenhua, Shanghai, China). The potential range of CV tests was from 0 V to 0.55 V, and the frequency range of EIS was from 10^{-2} Hz to 10^5 Hz with the amplitude of 5 mV.

3. Results and discussion

3.1. Structure and morphology

The XRD patterns of NiCo₂O₄@rGO/NF composites with different concentration of GO (3, 4, 5 and 6 mg mL⁻¹) are shown in Fig. 2. The diffraction peaks of the composites obtained at different concentrations of GO are basically the same. It indicates that the amount of GO in the preparation of the composites had no effect on the phase of NiCo₂O₄. Three strong and sharp diffraction peaks are corresponded to nickel deriving from the foam nickel substrate. The diffraction peaks of 2θ at 36.7° , 44.6° , 59.1° and 64.9° can be indexed to NiCo₂O₄ (JCPDS 20-0781), corresponding to (311), (400), (511) and (440) crystal planes, respectively. There is no obvious diffraction peak of rGO observed, which probably because the characteristic peak of rGO was covered by three strong peaks of nickel.³⁶ The chemical states of NiCo₂O₄@rGO/NF (GO 5 mg L⁻¹) are characterized by



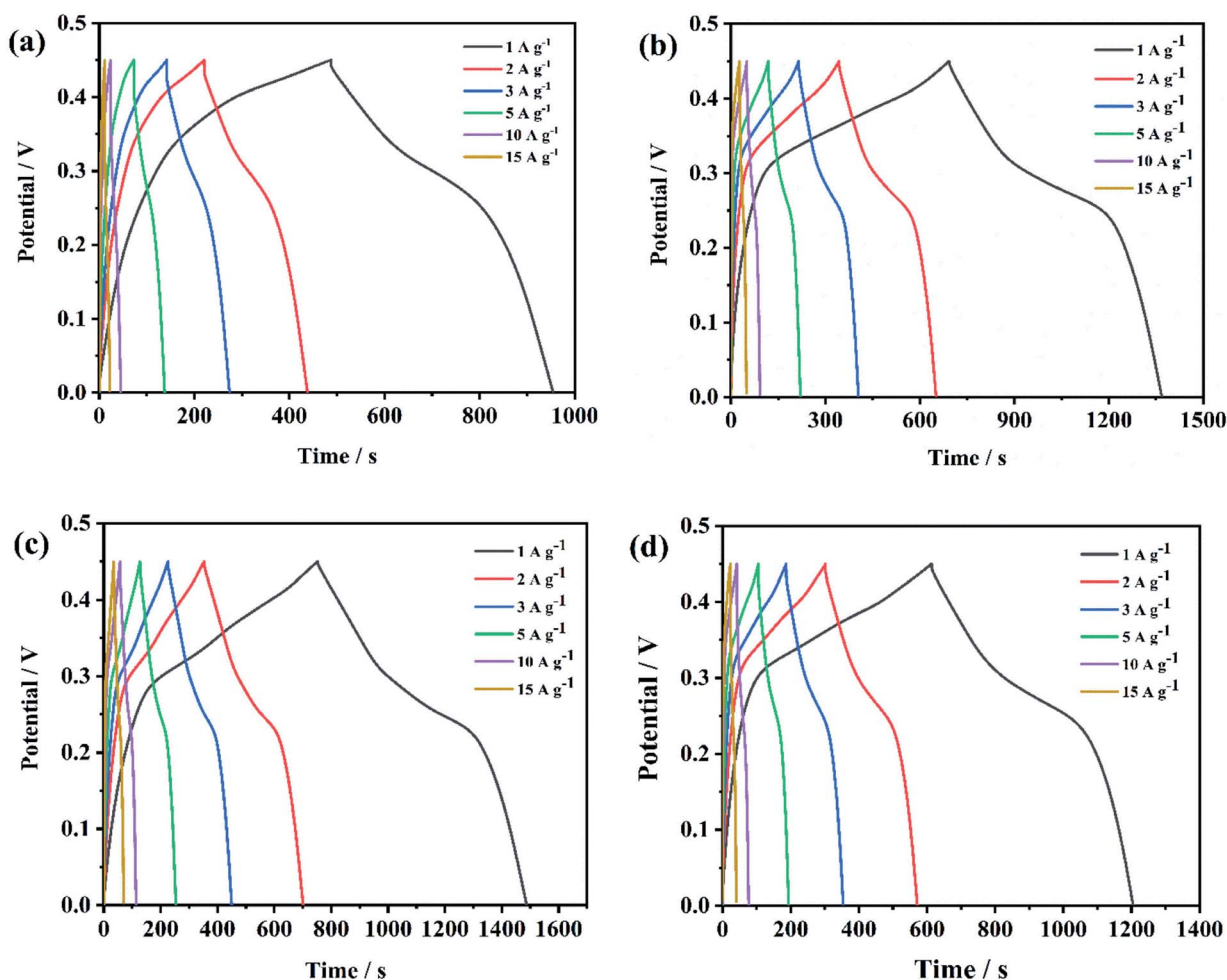


Fig. 8 GCD curves of NiCo₂O₄@rGO/NF with different concentration of GO at various current densities: (a) NiCo₂O₄@rGO/NF (GO 3 mg L⁻¹), (b) NiCo₂O₄@rGO/NF (GO 4 mg L⁻¹), (c) NiCo₂O₄@rGO/NF (GO 5 mg L⁻¹) and (d) NiCo₂O₄@rGO/NF (GO 6 mg L⁻¹).

XPS, as shown in Fig. 3, the region spectra of Ni 2p, Co 2p, O 1s and C 1s show characteristic peaks. The Ni 2p shows the peaks of Ni 2p_{3/2} and Ni 2p_{1/2} (Fig. 3(a)), both consisting of doublet peaks at 853.8, 855.4, 871.4 and 873.1 eV, corresponding to Ni²⁺ 2p_{3/2}, Ni³⁺ 2p_{3/2}, Ni²⁺ 2p_{1/2}, and Ni³⁺ 2p_{1/2}, respectively,³⁷ which could imply the presence of both Ni²⁺ and Ni³⁺. Two fitting peaks corresponding to Co 2p_{3/2} and Co 2p_{1/2} were observed in the Co 2p spectrum (Fig. 3(b)), which are characteristic of Co²⁺ and Co³⁺. The doublet peaks at 779.65 and 781.1 eV correspond to Co³⁺ 2p_{3/2} and Co³⁺ 2p_{1/2} as well as the other two at 794.85 and 796.65 eV correspond to Co²⁺ 2p_{3/2} and Co²⁺ 2p_{1/2}.³⁸ The spectrum of O 1s region (Fig. 3(c)) can be deconvoluted into four peaks at 529.15, 529.75, 531.25 and 532.3 eV, represented as O₁, O₂, O₃ and O₄, which are assigned to metal-oxygen bonds in the lattice of NiCo₂O₄, the surface hydroxyl, defect sites and physical/chemical adsorbed water, respectively.^{39,40} The C 1s spectrum (Fig. 3(d)) displays three types carbon bonds, including sp² C-C (284.8 eV), C-O (286.2 eV) and C=O (288.0 eV).⁴¹ It also can be seen from the peak intensity that the amount of oxygen-containing functional groups is less than that of C-C groups, indicating the successful reduction of GO to rGO.⁴⁰

The morphologies and nanostructures of bare Ni foam, NiCo₂O₄/NF and NiCo₂O₄@rGO/NF with different concentrations of GO (3, 4, 5 and 6 mg L⁻¹) are characterized by SEM and the images are shown in Fig. 4. As shown in Fig. 4(a and b), the surface of bare Ni foam is smooth. After hydrothermal reaction, double hydroxides precursor of NiCo₂O₄ was formed, which presents nanowire morphology (Fig. S1, ESI†). After heat treatment, when GO was in absence, the NF is completely covered by NiCo₂O₄ nanoneedle arrays, which are neatly oriented (Fig. 4(c and d)). When GO was added, the product of NiCo₂O₄@rGO still maintains nanoneedle morphology. However, it's important to point out that the nanoneedles crossed in different directions, as shown in Fig. 4(e-h). The difference in morphology is mainly due to the role of rGO. NF provided growth sites for NiCo₂O₄, and then nanoneedles' growth was prolonged and strongly isotropic. In the presence of rGO, rGO adsorbed to NF and then coated and separated NiCo₂O₄, which changed its growth direction and led to the anisotropy. As the concentration of GO increased, rGO cladding layers in the composites would be thickened. Fig. 5(a and b) show different magnified TEM images of NiCo₂O₄@rGO composites (GO 5 mg L⁻¹), from which it



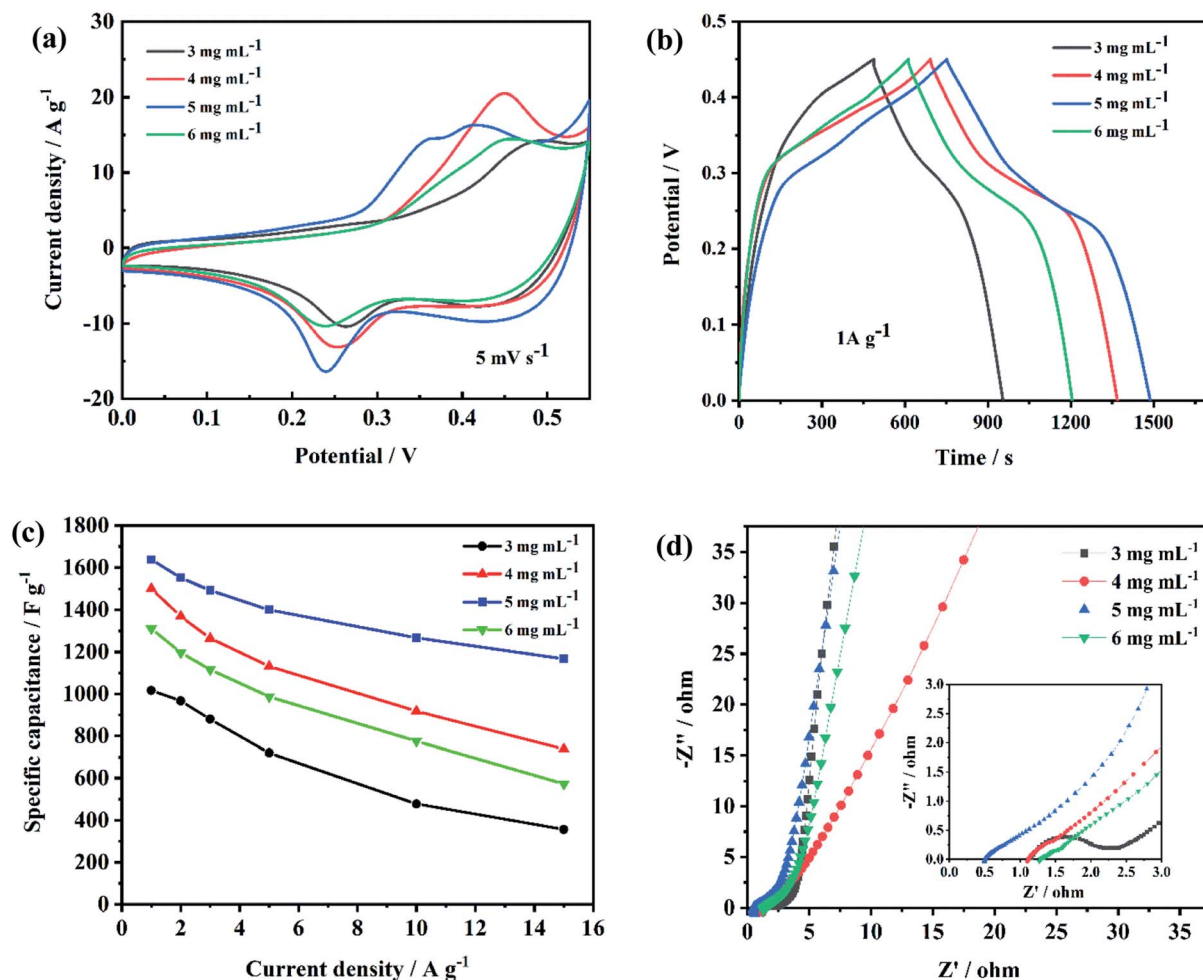
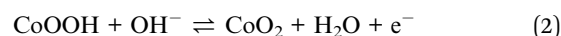


Fig. 9 Comparison of electrochemical performance of NiCo₂O₄@rGO/NF with different concentration of GO: (a) CV curves (5 mV s⁻¹), (b) GCD curves (1 A g⁻¹), (c) specific capacitances at various current densities and (d) Nyquist plots of EIS.

could be clearly observed that NiCo₂O₄ nanoneedles are interlaced. From HRTEM images (Fig. 5(c and d)), it can be seen that a lattice spacing of 0.458 nm corresponding to the (111) crystal plane of NiCo₂O₄. The SEM energy dispersive spectroscopy (EDS) in Fig. 6(a) verifies the existence of C, O, Ni and Co elements. As can be seen from the SEM (Fig. 6(b)) mapping images in Fig. 6(c), Co, Ni, C, and O distribute homogeneously over the NiCo₂O₄@rGO architecture. It also proves the existence and distribution of rGO in the composites.

3.2. Electrochemical performance

Fig. 7 shows CV curves of NiCo₂O₄@rGO/NF with different concentration of GO (3, 4, 5, 6 mg L⁻¹), which were carried out at the potential window from 0 to 0.55 V with the scan rate of 5, 10, 20, 30, 40 and 50 mV s⁻¹. There is a pair of redox peaks can be observed on all CV curves (Fig. 7(a-d)), which resulted from redox reactions of Co³⁺/Co⁴⁺, Ni²⁺/Ni³⁺ and Co²⁺/Co³⁺, demonstrating the pseudocapacitive characteristic of NiCo₂O₄@rGO/NF composite.⁴² The reaction equations are as follows:⁴³



When the scan rate increased from 5 to 50 mV s⁻¹, the shape of CV curves had little change, suggesting good electrochemical reversibility as supercapacitor electrodes. GCD curves of NiCo₂O₄@rGO/NF with different concentration of GO (3, 4, 5, 6 mg L⁻¹) at the various current density of 1, 2, 3, 5, 10 and 15 A g⁻¹ are displayed in Fig. 8. From (Fig. 8(a)-(d)) can we see, the charge-discharge curves are all nonlinear with evident voltage plateau, indicating typical pseudocapacitive behavior, which is consistent with the CV results. For a comparison, the electrochemical performance of NiCo₂O₄@rGO/NF composites with different concentration of GO were contrasted and depicted in Fig. 9. When the concentration of GO was 5 mg L⁻¹, the closed area of CV curve is the largest (Fig. 9(a)) and the GCD curve has the longest discharge time (Fig. 9(b)). The specific capacitance calculated by the GCD curve is 1044, 1504, 1644 and 1322 F g⁻¹, corresponding to GO concentration of 3, 4, 5 and 6 mg L⁻¹, respectively. At all the current densities, NiCo₂O₄@rGO/NF (GO 5 mg L⁻¹) has the largest specific capacitance compared with the samples of the other three concentrations.



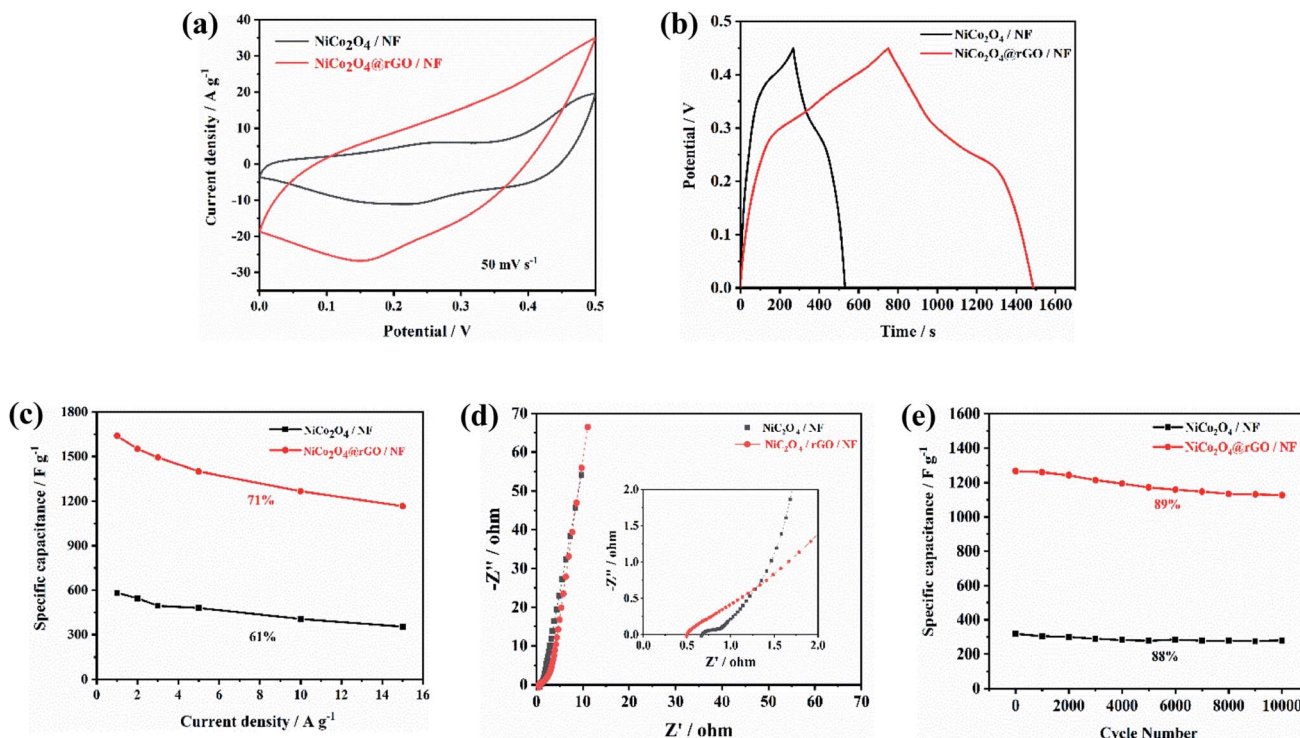


Fig. 10 Comparison of electrochemical performance of NiCo₂O₄@rGO/NF with NiCo₂O₄/NF: (a) CV curves (50 mV s⁻¹), (b) GCD curves (1 A g⁻¹), (c) specific capacitances at different current densities, (d) Nyquist plots of EIS and (e) cycling stability (10 A g⁻¹).

Moreover, its specific capacitance varies most gently with the current density, suggesting good rate performance (Fig. 9(c)). It is probably because that as the concentration of GO increased, the proportion of rGO in NiCo₂O₄@rGO/NF composite increased, and rGO plays a role in connecting NiCo₂O₄ nanoneedles to improve the electrical conductivity of the composite. However, due to the low specific capacitance of rGO itself, too much rGO will affect the overall specific capacitance of the composite. Nyquist plots of EIS for NiCo₂O₄@rGO/NF composites with various concentrations (3, 4, 5 and 6 mg L⁻¹) are shown in Fig. 9(d). The line at low frequency region of NiCo₂O₄@rGO/NF (GO 5 mg L⁻¹) is more vertical to the real axis (Z'), indicating more ideal capacitance behavior.⁴⁴

Fig. 10 describes the comparison of electrochemical properties of NiCo₂O₄@rGO/NF and NiCo₂O₄/NF. As shown in Fig. 10(a), the CV curves of NiCo₂O₄@rGO/NF and NiCo₂O₄/NF at the scan rate of 50 mV s⁻¹, NiCo₂O₄@rGO/NF has larger closed area than NiCo₂O₄/NF, demonstrating higher specific capacitance. It is confirmed by GCD tests, displayed in Fig. 10(b). At the current density of 1 A g⁻¹, the specific capacitance of NiCo₂O₄/NF and NiCo₂O₄@rGO/NF is 582.2 and 1644 F g⁻¹, respectively. Obviously, it is nearly twice higher the composite with rGO than that without rGO. Fig. 10(c) shows the specific capacitance of these two composites changing with the current density. The calculated specific capacitance of NiCo₂O₄@rGO/NF is 1644, 1551, 1493, 1400, 1267 and 1167 F g⁻¹ at the current density of 1, 2, 3, 5, 10 and 15 A g⁻¹. Even at 15 A g⁻¹, 71% of the specific capacitance (1 A g⁻¹) has still been retained, while the specific capacitance retention of NiCo₂O₄/NF is 61%. It can be

seen that NiCo₂O₄@rGO/NF has better rate performance. Nyquist plots of EIS for NiCo₂O₄@rGO/NF and NiCo₂O₄/NF are shown in Fig. 10(d). The intercept at the real axis represents the equivalent series resistance (R_s), containing the electrolyte resistance, the intrinsic resistance and the contact resistance. The diameter of the semicircle at the high frequency is associated with the charge-transfer resistance (R_{ct}). For NiCo₂O₄@rGO/NF and NiCo₂O₄/NF electrodes, the R_s values are 0.679 and 0.501 Ω , respectively, indicating that a lower solution resistance of NiCo₂O₄@rGO/NF than that of NiCo₂O₄/NF. Likewise, NiCo₂O₄@rGO/NF has a smaller semicircle, which could provide a fast pathway for ion transfer and electron transport. The cycle stability of the two electrodes after 10 000 cycles was tested at a current density of 10 A g⁻¹. As shown in Fig. 10(e), it is obvious that the specific capacitance of NiCo₂O₄@rGO/NF composite is much higher than that of NiCo₂O₄/NF. Additionally, NiCo₂O₄@rGO/NF can still maintain 89% of the initial specific capacitance after 10 000 charge-discharge cycles, exhibiting more excellent cycle stability than NiCo₂O₄/NF. The electrochemical properties of NiCo₂O₄ and its composite materials reported in some literatures are listed in Table 1. It can be seen from the literature comparison, the NiCo₂O₄@rGO/NF composite prepared in this work is comparable. In brief, the superiority of electrochemical performance of NiCo₂O₄@rGO/NF composite is mainly analyzed for the following reasons: (i) the anisotropic nanoneedles formed a cross network, which could provide an effective channel for ion/electron diffusion. (ii) NiCo₂O₄ grows directly on NF matrix, and rGO plays a bridge among the NiCo₂O₄ nanoneedles, together with no binder is used, which have effectively improve the conductivity of



Table 1 Comparison of electrochemical performance of NiCo₂O₄@rGO/NF in this work with previous literatures

Materials	Specific capacitance	Cycle stability	Rate performance	References
rGO/NiCo ₂ O ₄	1248 F g ⁻¹ (2 mA cm ⁻²)	90% (5 mA cm ⁻²) 2000 cycles	59% (2–10 mA cm ⁻²)	30
NiCo ₂ O ₄ nano-needles/NF	1410 F g ⁻¹ (1 A g ⁻¹)	94.7% (20 A g ⁻¹) 3000 cycles	73.8% (1–20 A g ⁻¹)	31
NiCo ₂ O ₄ /rGO	1380 F g ⁻¹ (1 A g ⁻¹)	90% (5 A g ⁻¹) 1000 cycles	70% (1–10 A g ⁻¹)	32
rGO@NiCo ₂ O ₄ NFs	1040 F g ⁻¹ (1 A g ⁻¹)	88% (30 A g ⁻¹) 5000 cycles	88.8% (1–10 A g ⁻¹)	45
NiCo ₂ O ₄ @NF	646.6 F g ⁻¹ (1 A g ⁻¹)	96.5% (7 A g ⁻¹) 3000 cycles (ASC)	32% (1–9 A g ⁻¹)	46
NiCo ₂ O ₄ @rGO/NF	1644 F g ⁻¹ (1 A g ⁻¹)	89% (10 A g ⁻¹) 10 000 cycles	71% (1–15 A g ⁻¹)	This work

the composite, due to the excellent electrical conductivity of NF and rGO. Furthermore, it also plays a positive role in the full use of active materials. (iii) The outstanding mechanical property inhibits the deformation caused by swelling/shrinking of the electrode material during the repeated charge–discharge process.

In addition, the asymmetric supercapacitor cell (ASC) was fabricated from two-electrode devices by using the prepared NiCo₂O₄@rGO/NF as the positive electrode and graphene hydrogel (GH) as the negative electrode in 6 M KOH electrolyte, illustrated in Fig. 11(a). As shown in Fig. 11(b), the CV curve of NiCo₂O₄@rGO/NF positive electrode exhibits a potential range of 0 V to 0.55 V, whereas that of GH negative electrode shows

a range of −1.0 V to 0 V. Therefore, CV measurements of NiCo₂O₄@rGO/NF//GH ASC were carried out at an operating potential window of 0 V to 1.55 V with the scan rate of 5, 10, 20, 50 and 100 mV s⁻¹ (Fig. 11(c)), which indicate that the CV curves at all the scan rates retain both the pseudocapacitive characteristic and electrochemical double layer capacitance (EDLC). Besides, the redox peak has a slight movement with the increase of the scan rate, perhaps owing to the electrode polarization.⁴⁷ Fig. 11(d) depicts GCD curves of NiCo₂O₄@rGO/NF//GH ASC at various current densities on the potential window of 0 V to 1.55 V. With the increase of the current density, the curves could maintain an approximate symmetrical triangle, showing good

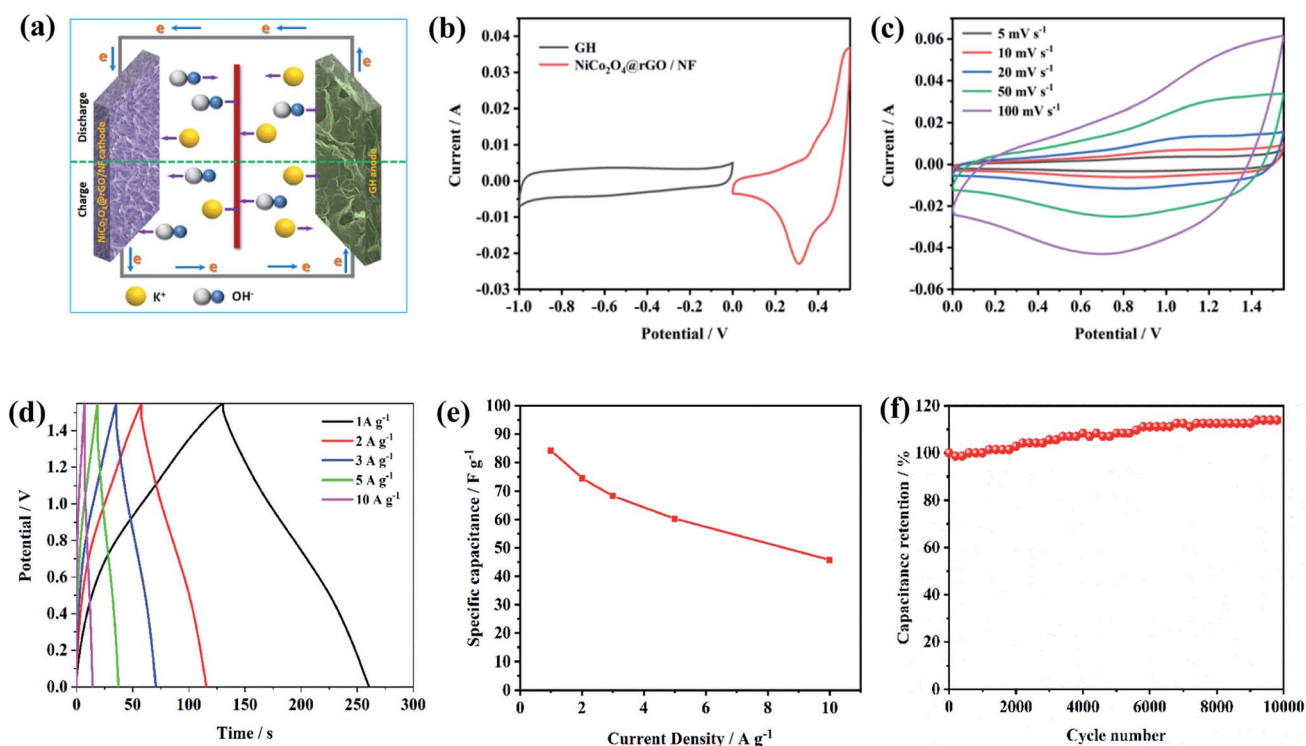


Fig. 11 (a) Schematic of the fabricated NiCo₂O₄@rGO/NF//GH asymmetric supercapacitor device, (b) CV curves of GH anode and NiCo₂O₄@rGO/NF cathode electrodes (5 mV s⁻¹), (c) CV curves of NiCo₂O₄@rGO/NF//GH at various scan rates, (d) GCD curves of NiCo₂O₄@rGO/NF//GH at various current densities, (e) specific capacitances of NiCo₂O₄@rGO/NF//GH at various current densities and (f) cycling performance of NiCo₂O₄@rGO/NF//GH device (10 A g⁻¹).



reversibility. The calculated specific capacitance of the ASC device is 84.13, 74.58, 68.32, 60.32 and 45.81 F g⁻¹ at the current density of 1, 2, 3, 5 and 10 A g⁻¹, respectively. The rate performance of NiCo₂O₄@rGO/NF//GH ASC is displayed in Fig. 11(e). When the current density increased to 10 A g⁻¹, it could still maintain 54.5% of the specific capacitance at 1 A g⁻¹. Fig. 11(f) describes the cycle performance of NiCo₂O₄@rGO/NF//GH ASC at a current density of 10 A g⁻¹. After 10 000 cycles, the specific capacitance increased to 51.76 F g⁻¹, which is 113% of the initial value (45.81 F g⁻¹), which is probably because of the electrolyte has fully penetrated into the material, making the active material be more fully utilized with the continuous charge–discharge cycles, demonstrating excellent cycle stability of NiCo₂O₄@rGO/NF//GH ASC device.

4. Conclusion

In conclusion, NiCo₂O₄@rGO/NF composite electrode materials with enhanced supercapacitive performance were synthesized by a simple hydrothermal method assisted by CTAB combined with subsequent heat treatment. The aeolotropic NiCo₂O₄@rGO nanoneedles grew directly on Ni foam with rGO connecting to each other and without any binder, which has greatly improved the conductivity of electrode materials. Moreover, the crossed network also provides a pathway for ion diffusion. For supercapacitor application, the highest specific capacitance of NiCo₂O₄@rGO/NF could reach 1644 F g⁻¹ at a current density of 1 A g⁻¹, and even at 15 A g⁻¹, the value still maintain 1167 F g⁻¹, additionally, there is 89% capacitance retention after 10 000 cycles at 10 A g⁻¹. Furthermore, NiCo₂O₄@rGO/NF//GH ASC device was assembled and exhibits a high specific capacitance of 84.13 F g⁻¹ (1 A g⁻¹) and excellent cycle stability (113% capacitance retention after 10 000 charge/discharge cycles at 10 A g⁻¹). Higher specific capacitance, better rate performance and cycle stability highlight the advantages of NiCo₂O₄@rGO/NF composites as electrode materials for supercapacitors, associating with the regulated morphology, suitable GO concentration synergy of components. As one of the most promising materials, it is believed that NiCo₂O₄@rGO/NF will have a broader application prospect in the future.

Conflicts of interest

There are no conflicts to declare.

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