Nanoneedle-like NiCo₂O₄ Decorated Carbon Nanofiber Electrodes for Supercapacitors

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Abstract. Flexible electrodes based on carbon fiber with excellent conductivity were utilized in supercapacitor applications. Herein, the nanostuctured NiCo₂O₄ was synthesized along the nanofibers by a brief hydrothermal method. As-prepared NiCo₂O₄/CNF composite holds unique structure with NiCo₂O₄ nanoneedles uniformly grown on every carbon nanofiber, which promised shorter diffusion of electrons and ions. The composite electrode held a high capacitance of 660.41 F g⁻¹ and showed great capacitance retention of 90.95% after 6000 cycles, which could be beneficial in future application of supercapacitors.

1. Introduction
At present, with limit of fuel energy resources and enormous energy demands for daily production¹¹, the research on more renewable devices with high energy storage properties attracted great efforts actively². Supercapacitors, also called electrochemical capacitors, have great potential due to outstanding characteristics like high energy density, fast exchange rate and long cycle life³. In general, considering their energy storage mechanism, supercapacitors can be divided to two kinds including electrical double-layer capacitors (EDLCs) and pseudocapacitors⁴, ⁵. Carbon materials are in common use as electrodes in electrochemical capacitors because of their good conductivity and huge surface area for ion adsorption and diffusion⁶, ⁷. Among them, the carbon nanofiber is considered as an outstanding alternative for high-performance supercapacitors because the interconnected framework with stable properties enlarge the surface area and also prevent aggregation and probabilities of swelling during the activation. Through the reversible and rapid reactions, pseudocapacitors can store the charges from the active materials and provide higher capacitance⁷. Transition metal oxides⁸, sulfides⁹, conducting polymers, due to highly efficient energy storage performance, have aroused much attention. Among various metal oxides, binary nickel cobalt oxide(NiCo₂O₄) is reported as one of the most important candidates with such advantages as high theoretical capacitance (>3000 F g⁻¹), better conductivity¹⁰, low cost and huge abundance in nature. Therefore, many researchers have committed to fabricate free-standing electrode of robust electrochemical property combined with pseudocapacitive active materials and carbon materials to develop their synergistic performance¹¹. It is also beneficial to avoid volume expansion properties during reversible reaction¹², ¹³. Long Chen¹⁴ designed metal nanoparticles decorated NiCo₂O₄ along carbon nanofibers, exhibiting 781 F g⁻¹. Qi Tang¹⁵ prepared a N-doped porous carbon/NiCo₂O₄ (NPC/NiCo₂O₄) with high capacitance of 948.30 F g⁻¹ at 1 A g⁻¹. Herein, nanoneedle-like NiCo₂O₄/CNF composite is prepared by two step reactions. Firstly, using P(AN-co-MHI) copolymer as precursor, we fabricated flexible carbon fiber to reduce
defects in final CNF from the heat release during the stabilization of PAN solely. Then, the flexible free-standing NiCo$_2$O$_4$/CNF composite was obtained through a facile hydrothermal process. As prepared electrode composite possesses distinguished electrochemical behavior and thus proved of great importance as promising electrode material for flexible supercapacitors.

2. Experimental

2.1. Materials
Nickel nitrate hexahydrate(Ni(NO$_3$)$_2$·6H$_2$O), cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O), urea, N,N-dimethylformide (DMF), and potassium hydroxide (KOH) were purchased from Aladdin Co. Ltd. (China). All other reagents were of analytical grade and used without further purification. Poly(acrylonitrile-co-β-methylhydrogen itaconate) (P(AN-co-MHI)) was synthesized as precursor according to previous paper[16].

2.2. Preparation of CNFs
(P(AN-co-MHI) was dissolved in DMF as the precursor solution with the concentration of 18% and a homogeneous transparent solution was obtained by mild stirring for several hours at 60 °C. Then about 8 ml solution was shifted to a 10 ml syringe to fabricate nanofiber in a syringe pump maintained with a feeding rate at 0.6 mL/ h. The electrospinning was carried out at 13.67 kV with 20 cm from collector to tip. Afterwards, the obtained nanofiber membranes were preoxidized under 290℃ for 2 h in air atmosphere and then further carbonized under N$_2$ atmosphere from room temperature to 1000 °C that maintained a heating rate of 5 °C /min.

2.3. Preparation of NiCo$_2$O$_4$ decorated CNF composite electrodes
The NiCo$_2$O$_4$/CNF composite electrodes were prepared by a simple hydrothermal reaction. 5 mM Ni(NO$_3$)$_2$·6H$_2$O, 10 mM Co(NO$_3$)$_2$·6H$_2$O, 8 mM urea and 35 ml deionized water were added together and dissolved with continuous stirring. After shifting the mixture into a 50 ml Teflon-lined stainless steel autoclave, the CNF was immersed in the solution and kept at 120 °C for 10 h. After reaction, the as-prepared CNF was washed with deionized water for several times and dried at 60°C. After that, the precursor composite nanofiber was put in N$_2$ atmosphere under 350 ℃ for extra 2h to obtain NiCo$_2$O$_4$ decorated CNF composite.

2.4 Characterization
The surface morphology of the composites was characterized by FESEM (S-4800, Hitachi). X-ray powder diffraction (XRD) was used for the crystal phases on a Rigaku D/max-2550 diffractometer between 0-80° at the rate of 3° /min while X-ray photoelectron spectroscopy (XPS, Escalab 250Xi) used for the elements composition examination. The electrochemical characterization of the samples was measured in a three-electrode cell by a electrochemical workstation (Ivium Technologies) in 2M KOH solution. Cyclic voltammetry (CV) tests and the EIS measurements were performed with a potential range from 0 to 0.45 V and in the frequency range from 0.01 Hz-100 kHz at an open potential, respectively.

3. Results and discussion

Fig 1. The preparation of the NiCo$_2$O$_4$/CNF composite electrodes
The preparation process of NiCo$_2$O$_4$/CNF was illustrated in Fig.1 according to 3 brief steps. Firstly, CNF was obtained through electrospinning, stabilization and annealing. Afterwards, facile hydrothermal synthesis was carried out to produce NiCo-precursor on the CNFs. Eventually, uniformly covered NiCo$_2$O$_4$ nanoneedles were grown uniformly along the CNFs.

Fig.2. SEM images of (a) bare CNF (b)(c) NiCo$_2$O$_4$/CNF composite

Fig.2 (a) – (c) showed the morphology and structure of the NiCo$_2$O$_4$/CNF composite. The fresh carbon nanofiber was smooth and exhibited an average diameter of 550-560 nm in Fig 2 (a). From the low magnification images, the crisscross framework of carbon fibers is beneficial to form a porous network, offering more efficient ion and electron diffusion channels. Fig 2 (b) showed the nanoneedle-like structure of NiCo$_2$O$_4$ was obtained successfully on the CNFs with a hierarchical array feature. Moreover, from Fig.2 (c), the high magnification SEM figures indicated that the average diameter of the NiCo$_2$O$_4$ nanoneedle was about 250-300nm, which was good for the movements of the electrolyte, contributing to the optimization of electrochemical performance.

The diffraction patterns were further analyzed by XRD pattern. Fig.3 showed the XRD curves of NiCo$_2$O$_4$/CNF composite and NiCo$_2$O$_4$ as well. All the characteristic peaks showed at 2θ = 18.93°, 31.15°, 36.71°, 44.60°, 59.21° and 64.90° showed good agreement with (111), (220), (311), (400), (511) and (440) crystal planes of NiCo$_2$O$_4$(JCPDS,20-0781) respectively[17]. Meanwhile, without other impurity peaks, indicating that the NiCo$_2$O$_4$/CNF composite was prepared with high purity.

Fig.3 (a)X-ray diffraction patterns of NiCo$_2$O$_4$/CNF composite and bare NiCo$_2$O$_4$; XPS curves of NiCo$_2$O$_4$/CNF composite electrode (b) O1s (c) Co 2p (d) Ni 2p
More detailed surface information was further analyzed by X-ray photoelectron spectroscopy (XPS) of the NiCo$_2$O$_4$/CNF composite sample. The binding energies at 530.9 eV, 531.5 eV and 533.6 eV were in agreement with three typical states including -C=O, C-O-C, O-C=O [18] for the O atom from O 1s spectrum in Fig. 3 (b). Fig. 3 (c) exhibited Co 2p spectra with two obvious peaks seen at 789.3 eV and 795.1 eV, regarded as typical Co$^{2+}$ species. Other two peaks at 780.9 eV and 795.5 eV were corresponded to Co$^{3+}$. Besides, their two shake-up satellite peaks (identified as “Sat.”) were also shown clearly in the spectra [19]. The main peaks at binding energies of 854.9 eV, 872.7 eV and 861.9 eV, 879.2 eV fitted well with Ni$^{2+}$ and Ni$^{3+}$ species respectively. Two shake-up satellites were also found obviously in Ni 2p spectra (Fig.3 (d)). The carbon nanofiber was synthesized successfully with NiCo$_2$O$_4$ decoration from the coexistence of multi-elements (Ni, Co, O). The electrochemical properties of NiCo$_2$O$_4$/CNF composite were examined by galvanostatic charge/discharge tests, cyclic voltammetry, Nyquist plot and cyclic stability in 2M KOH solutions. Fig.4 (a) demonstrated the CV spectrums of the as-obtained electrode at different scan rate (5, 10, 20, 40 mV s$^{-1}$). Two sensitive redox peaks are visibly observed at 0.13 V and 0.4 V, which are caused by redox reactions as follows [20]:

$$\text{NiCo}_2\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \rightleftharpoons \text{NiOOH} + 2\text{CoOOH} + e^- \quad (1)$$

$$\text{CoOOH} + \text{OH}^- \rightleftharpoons \text{CoO}_2 + \text{H}_2\text{O} + e^- \quad (2)$$

![CV patterns](image1)

As is shown, the position of the peaks changed according to the scanning rate. Because of the polarization phenomenon, the reduction peaks deviated to lower negative potential while the oxidation peaks shift to higher positive potential [21]. According to the previous literature, it could be attributed to the mechanism for ion activation and redox reaction on the electrode surface. At higher speed, electrolyte ions failed to have enough time to make diffusion and penetration with the active nanoneedle materials on the surface fully and completely, leading to a reduction in pseudocapacitive capacitance.
The galvanostatic charge-discharge spectrums of NiCo$_2$O$_4$/CNF composite was illustrated in Fig.4 (b) between the potential from 0 to 0.45 V under current densities range from 0.5 A g$^{-1}$ to 4.0 A g$^{-1}$, respectively. The symmetric-like curves, suggesting excellent reversible faradic characteristics. At around 0.29 V, a voltage plateaus was obtained, indicating a typical pseudocapacitive properties. The following formula was used to calculate the specific capacitance $C$ (F g$^{-1}$) of NiCo$_2$O$_4$/CNF composite:

$$C = \frac{It}{m\Delta V}$$ (3)

where $I$(A) and $\Delta V$(V) are discharge current and potential range, $t$(s) is the discharge time, and $m$(g) denotes the weight of active material.

The specific capacitance could be calculated to 660.41 F g$^{-1}$ at the current density of 0.5 A g$^{-1}$ in Fig.4 (b). Fig.4 (c) described the cyclic stability of the NiCo$_2$O$_4$/CNF composite after 6000 cycles of charging and discharging measurements. The composite electrode sample displayed an excellent cyclability with almost 90.95% capacitance retention. The inset of Fig.4 (c) demonstrated the GCD tests of the electrode with a current density of 4 A g$^{-1}$ at first ten cycles. The significant capacitance of composite electrode could be attributed to the satisfactory combination of the carbon nanofibers as well as the unique structure. The cross-linked framework of conductive CNF promised strong support with huge surface area for the growth of active NiCo$_2$O$_4$. Meanwhile, the superior structure also prevented the agglomeration of NiCo$_2$O$_4$. Moreover, the combination of the network and the evenly NiCo$_2$O$_4$ nanoneedle structure shortened the transport pathway and made the migration of electrons faster. The Nyquist plots were implemented with a semicircle in the high frequency region under an open circuit voltage in Fig.4 (d), reflecting the charge-transfer resistance during iron diffusion$^{[22]}$. The internal resistance of NiCo$_2$O$_4$ nanoneedle decorated CNF electrode was 4.92 $\Omega$. The small Rct contributed greatly to the transfer of electron quickly. At the same time, the slope of the EIS spectrum in low frequency was shown in a linear shape, displaying higher electron diffusion on the surfaces of electrodes, which is greatly good for the high electrochemical properties of NiCo$_2$O$_4$/CNF composite.

4. Conclusion

In summary, the NiCo$_2$O$_4$/CNF composite electrode was prepared successfully by a simple hydrothermal reaction. The as obtained NiCo$_2$O$_4$/CNF composite with specific nanoneedle-like structure, which offered large surface area with shorter ion diffusion distances, possessed an excellent electrochemical behavior with great capacitance of 660.41 F g$^{-1}$ at 0.5 A g$^{-1}$. Meanwhile, after 6,000 cycles, the retention property still remained 90.95% of the initial performance. Overall, NiCo$_2$O$_4$/CNF composite could be a promising electrode material applied in supercapacitor.

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