A high performance symmetrical supercapacitor based on NiCo$_2$O$_4$ nanowires on thin film carbon layer

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Abstract Here we proposed novel NiCo$_2$O$_4$ nanowires on carbon black layer that used as a superior electrode for supercapacitors, with an excellent pseudocapacitive performance. The NiCo$_2$O$_4$ nanowires-based electrode provide high values of specific capacitance of 3.31 F/cm$^2$ corresponding to the current densities of 5 mA/cm$^2$. The symmetrical supercapacitor based on NiCo$_2$O$_4$ nanowires-based electrode have a high areal specific capacitance of 42.6 mF/cm$^2$ corresponding to the current densities of 0.5 mA/cm$^2$. It exhibited good cycling life that the specific capacitance maintained with no decrease during 50000 cycles. Our work can be applied in mass applications of high-capacitance energy-storage supercapacitors.

1. Introduction
At present, due to the rapid charging capability, high power density, and long working life of supercapacitors, supercapacitors have attracted wide attention as promising energy storage and power output devices comparable to batteries. [1-3] However, their capacity is still lower than that of batteries, and their good performance environments are generally limited to liquid electrolytes, which severely limits their practical application in terms of flexibility, portability, miniaturization, and integrated electronic devices. [4-8] Therefore, while increasing the capacity, the construction of an all-solid-state supercapacitor is concentrated as one of the core issues in realizing a high-performance supercapacitor.

Based on the charge storage mechanism, supercapacitors are generally classified into two types: double-layer capacitors and Faraday tantalum capacitors. [9-11] Faraday tantalum capacitors utilize reversible faradaic capacitances that occur on the load-transition metal oxide at or near the surface of the electrode. Regarding the research of tantalum capacitors, the hot spot in this area and the related development of the correct electrode materials, including the composition, structure, distribution, etc., are the transition metal oxides of nanostructures, such as NiCo$_2$O$_4$ and ZnCo$_2$O$_4$ are excellent supercapacitor electrode materials because of their good conductivity, large surface area and highly reactive oxidation state. [12-14] Recently, many advanced, advanced structural composites have been considered as potential supercapacitor candidates and have excellent performance in improving electrochemical performance.
Here we proposed novel NiCo$_2$O$_4$ nanowires on carbon black layer that used as a superior electrode for supercapacitors, with an excellent pseudocapacitive performance. The NiCo$_2$O$_4$ nanowires-based electrode provide high values of specific capacitance of 3.31 F/cm$^2$ corresponding to the current densities of 5 mA/cm$^2$. The symmetrical supercapacitor based on NiCo$_2$O$_4$ nanowires-based electrode have a high areal specific capacitance of 42.6 mF/cm$^2$ corresponding to the current densities of 0.5 mA/cm$^2$. It exhibited good cycling life that the specific capacitance maintained with no decrease during 50000 cycles.

2. Experimental section

*Materials Synthesis:* All the reagents in this experiment were purchased from Sinopharm Chemical Reagent Co. Ltd. First, a layer of pvp film was grown via electrospinning. Then a layer of carbon black powder was coated on pvp film, used as conductive electrode layer. Then the film was put in hydrothermal progress and then annealing to grow NiCo$_2$O$_4$ nanowires on electrode layer. Finally, two electrode and a layer of septum were put together to sandwich structure with PVA-KOH electrolyte, to form a full supercapacitor.

*Materials Characterization:* The obtained nanowires were examined by the X-ray diffraction (XRD; Cu target, $\lambda=0.15406$ nm) with a Bruker D8 Advance X-ray diffractometer. The surface morphology of the samples was characterized by a scanning electron microscopy (SEM; FEI NanoSEM650) and a transmission electron microscope (TEM; FEI Tecnai G2 F20 S-TWIN (200kV)). The electrochemical measurements were carried out with an electrochemical workstation (Chenhua, CHI 660D).

3. Results and Discussion

Figure 1 demonstrates the typical fabrication procedures for the NiCo$_2$O$_4$ nanowires-based electrode and the symmetrical supercapacitor. First, a layer of pvp film was grown via electrospinning. Then a layer of carbon black powder was coated on pvp film, used as conductive electrode layer. Then the film was put in hydrothermal progress and then annealing to grow NiCo$_2$O$_4$ nanowires on electrode layer. Finally, two electrode and a layer of septum were put together to sandwich structure with PVA-KOH electrolyte, to form a full supercapacitor.

![Figure 1](image)

**Figure 1.** The typical fabrication procedures for the NiCo$_2$O$_4$ nanowires-based electrode and the symmetrical supercapacitor.

Figure 2a-c shown the SEM images after the three steps of fabrication procedures. In Figure 2a, a pvp film was shown. The cabon black layer was then coated on pvp film, as shown in Figure 2b. And the nanowires obtained after the third step was displayed in Figure 2c. Products were characterized by X-ray diffraction (XRD) and shown in Figure 2d. Peaks at $2\theta = 31.15, 36.70, 44.62, 59.09$ and $64.98$ degrees in the patterns of NiCo$_2$O$_4$ were perfectly indexed to the (220), (311), (400), (511) and (440) planes of the cubic NiCo$_2$O$_4$ phase (JCPDS No. 20-0781). Figure 2e and 2f display the transmission
electron microscopy (TEM) image of the nanowire and its high-resolution TEM (HRTEM) image. The clearly resolved lattice fringes of about 0.47 nm was corresponding well to the (111) plane of cubic structured NiCo$_2$O$_4$. Above all, NiCo$_2$O$_4$ nanowires were grew directly on carbon layer to form plane electrode for supercapacitor.

**Figure 2.** (a-c) SEM images after the three steps of fabrication procedures; (d) XRD patterns of the obtained nanowires; (e) TEM image of the nanowires; (f) corresponding HRTEM image nanowires.

Electrochemical measurements of the NiCo$_2$O$_4$ nanowires-based electrode were carried out in a three-electrode electrochemical cell with 2 M KOH electrolyte. Figure 3a showed the cyclic voltammogram (CV) curves of NiCo$_2$O$_4$ nanowires electrode measured at scan rates ranging from 10 mV/s to 100 mV/s in a potential window of -0.3~0.6 V vs. Saturated Calomel Electrode (SCE). The CV curves showed redox peaks, indicating better faradic capacitive behavior. The introduction of the NiCo$_2$O$_4$ nanowires to construct the hierarchical structures increased drastically the specific surface areas and adding more active materials, which could increase the area specific capacitance.

**Figure 3.** (a) CV and (b) galvanostatic charge-discharge curves of the NiCo$_2$O$_4$ nanowires electrode; (c) the areal capacitances of the NiCo$_2$O$_4$ nanowires electrode at varied galvanostatic CD current densities.

Galvanostatic charge–discharge (CD) measurements were also carried out in the potential window from -0.2 to 0.4 V (vs. SCE) at current densities from 5 mA/ cm$^2$ to 50 mA/ cm$^2$. Then the capacitances
of the NiCo$_2$O$_4$ nanowires electrode was estimated. The CD curves were shown in Figure 3b. The specific capacitances of NiCo$_2$O$_4$ nanowires electrode evaluated from the discharge curves of Figure 3b were 3.31, 2.89, 2.49, 2.08, 2.00, 1.87, 1.74, 1.52 and 1.34 F/cm$^2$ corresponding to the current densities of 5, 10, 20, 30, 40, 50, 60, 70 and 80 mA/cm$^2$, respectively. And the corresponding faradic reactions could be described by the following equations: [15-17]

\[
\begin{align*}
\text{NiO} + \text{OH}^- & \leftrightarrow \text{NiOOH} + e^- \\
\text{CoO} + \text{OH}^- & \leftrightarrow \text{CoOOH} + e^- \\
\text{CoOOH} + \text{OH}^- & \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^-
\end{align*}
\]

Figure 4. (a) CV and (b) galvanostatic CD curves of the NiCo$_2$O$_4$ nanowires based symmetrical supercapacitor; (c) the areal capacitances of the symmetrical supercapacitor at these CD current densities; (d) cycle stability of the symmetrical supercapacitor at the current density of 5 mA/cm$^2$.

Then, a symmetrical supercapacitor was fabricated with two NiCo$_2$O$_4$ nanowires-based electrodes, cellulose paper as the separator and KOH-PVA as the colloidal electrolyte. The voltage window of this NiCo2O4 nanowires based symmetrical supercapacitor was 0–1 V. The CV curves of the supercapacitor at the scan rates of 10–200 mV/s were shown in Figure 4a. As the scan rate increased, more closed areas of the CV curves were augmentative while the shapes remained quasi-rectangular. Figure 4b displayed the CD curves of the supercapacitor. The areal specific capacitances evaluated from the CD curves were 42.6, 33.8, 28.7, 27.1, 26.1, 24.9, 23.9 and 18.9 mF/cm$^2$ corresponding to the current densities of 0.5, 1, 2, 3, 4, 5, 7 and 10 mA/cm$^2$, respectively, which were shown in Figure
4c. This supercapacitor displayed an excellent high capacitance as an energy-storage device. The working stability in thousands of cycles is requested for supercapacitors in real applications. The NiCo$_2$O$_4$ nanowires-based supercapacitor exhibited an outstanding long-cycle life that no decreasing of the capacitance of the supercapacitor appeared during 50000 times cycling, at the current density of 5 mA/cm$^2$, as shown in Figure 4d.

4. Conclusion

Overall, the novel NiCo$_2$O$_4$ nanowires on carbon black layer was used as a superior electrode for supercapacitors, with an excellent pseudocapacitive performance. The NiCo$_2$O$_4$ nanowires-based electrode provide high values of specific capacitance of 3.31, 2.89, 2.49, 2.08, 2.00, 1.87, 1.74, 1.52 and 1.34 F/cm$^2$ corresponding to the current densities of 5, 10, 20, 30, 40, 50, 60, 70 and 80 mA/cm$^2$, respectively. The symmetrical supercapacitor based on NiCo$_2$O$_4$ nanowires-based electrode have a high areal specific capacitance of 42.6, 33.8, 28.7, 27.1, 26.1, 24.9, 23.9 and 18.9 mF/cm$^2$ corresponding to the current densities of 0.5, 1, 2, 3, 4, 5, 7 and 10 mA/cm$^2$, respectively. It exhibited good cycling life that the specific capacitance maintained with no decrease during 50000 cycles.

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