Hierarchical NiCo$_2$O$_4$@NiCo$_2$S$_4$ Nanocomposite on Ni Foam as an Electrode for Hybrid Supercapacitors

Heng Rong, Tao Chen, Rui Shi, Yuanyuan Zhang, and Zhenghua Wang*

Key Laboratory of Functional Molecular Solids, Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, P. R. China

**ABSTRACT:** In this work, NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite with a hierarchical structure is prepared by a multistep process. First, NiCo$_2$O$_4$ nanowires array on Ni foam is prepared by a hydrothermal and a subsequent calcination process. Then, the NiCo$_2$O$_4$ nanowires array is converted to NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite through a vapor-phase hydrothermal process. The NiCo$_2$O$_4$@NiCo$_2$S$_4$/Ni foam electrode exhibits a specific capacitance of 1872 F g$^{-1}$ at 1 A g$^{-1}$, a capacitance retention of 70.5% at 10 A g$^{-1}$, and a retention ratio of 65% after 4000 charge–discharge cycles. The capacitance of NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite is much higher than that of the NiCo$_2$O$_4$ nanowires array. The excellent electrochemical capacitive performances of the NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite can be attributed to the hierarchical nanostructure, which can provide large surface areas and short diffusion pathways for electrons and ions. By using the NiCo$_2$O$_4$@NiCo$_2$S$_4$/Ni foam as the positive electrode and activated carbon/Ni foam as the negative electrode, a hybrid supercapacitor device is fabricated. The device achieves an energy density of 35.6 W h kg$^{-1}$ and a power density of 1.5 kW kg$^{-1}$ at 2 A g$^{-1}$.

**INTRODUCTION**

In recent years, with the rapid development of electric vehicles and consumer electronic products, the requirements for electrical energy storage devices are ever-growing. Supercapacitors and secondary batteries are regarded as major electrical energy storage devices. Compared with the widely used secondary batteries such as lithium-ion batteries, supercapacitors possess the advantages including high power density, long cycle life, and improved safety, but suffer from drawbacks such as low energy density. To meet the requirement of actual applications, much effort is still needed to improve the energy density of supercapacitors while maintaining a high power density and a long cycle life.

Electrode materials are decisive on the performance of supercapacitors. Transition metal oxides and sulfides such as NiCo$_2$O$_4$ and NiCo$_2$S$_4$ have been widely studied as electrode materials for supercapacitors. Unlike carbon materials, which store charges via electric double-layer mechanism, transition metal oxides and sulfides store charges via reversible faradic redox reactions, and can achieve much higher specific capacitances than that of carbon materials. As the faradic redox reactions mainly occur on the surface of electrode materials, it is necessary to develop electrode materials with large surface areas and short diffusion pathways for electrons and ions. Nanostructures such as nanosheets and porous nanowires have been well studied for supercapacitors because they can provide large surface areas and short diffusion pathways for electrons and ions. Recently, some hierarchical nanocomposite materials have been developed for supercapacitor applications. In the hierarchical nanocomposite materials, different materials with various nanostructures are combined together. The synergistic effects result in improved electrochemical performances than that of the individual constituents.

The energy density of supercapacitors is proportional to the square of working voltage, and a higher working voltage means a higher energy density. However, the working voltage of symmetric supercapacitor is restricted by the stable potential window of water when aqueous electrolyte is used. To increase the working voltage of supercapacitors, hybrid supercapacitors are developed. In hybrid supercapacitors, a faradic-type material acts as the positive electrode and a capacitor-type material acts as the negative electrode. Because of the different working mechanism of the positive and negative electrode materials, the working voltage of hybrid supercapacitors can be obviously increased. The development of high-performance electrode materials for hybrid supercapacitors is still of great interest.

In this work, a hierarchical core–shell NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite is synthesized by a multistep process. In the NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite, NiCo$_2$S$_4$ nanosheets are...
supported on NiCoO$_4$ porous nanowires. Owing to the excellent structural advantages such as large specific surface areas, short diffusion pathways, and absence of aggregation, the NiCo$_2$O$_4@$NiCo$_2$S$_4$ nanocomposite shows enhanced supercapacitor performances over NiCo$_3$O$_4$ porous nanowires. The hierarchical NiCo$_2$O$_4@$NiCo$_2$S$_4$ nanocomposite can be used as a high-performance electrode material for supercapacitor applications.

## RESULTS AND DISCUSSION

The synthesis of hierarchical NiCo$_2$O$_4@$NiCo$_2$S$_4$ nanocomposite was realized through a multistep process, as illustrated in Figure 1. First, a precursor was grown on Ni foam by using Ni(NO$_3$)$_2$, Co(NO$_3$)$_2$, and Co(NH$_2$)$_2$ as raw materials through a hydrothermal process. Then, the precursor was converted to NiCo$_2$O$_4$ through calcination under ambient atmosphere. Finally, NiCo$_2$O$_4@$NiCo$_2$S$_4$ nanocomposite was obtained by treating NiCo$_2$O$_4$ in the atmosphere of thioacetamide solution under hydrothermal condition. The composition of the products obtained at different stages is studied by X-ray diffraction (XRD) technique. The diffraction peaks in the XRD pattern of the precursor (Figure S1a, Supporting Information) can be indexed to Co$_2$(CO$_3$)$_3$(OH)$_2$·0.11H$_2$O (JCPDS card no. 48-0083) and Ni$_2$(OH)$_2$CO$_3$·H$_2$O (JCPDS card no. 38-0714). The XRD pattern of the product obtained by calcining the precursor under ambient atmosphere (Figure S1b) can be indexed to spinel NiCo$_2$O$_4$ (JCPDS card no. 73-1702). The formation of NiCo$_2$O$_4$ is a result of the decomposition and oxidation of the precursor through calcination. The XRD pattern of the final NiCo$_2$O$_4@$NiCo$_2$S$_4$ sample is shown in Figure 2. In addition to the diffraction peaks of NiCo$_2$O$_4$, some weak diffraction peaks of NiCo$_2$S$_4$ are also present. This can be attributed to the low content and poor crystallinity of NiCo$_2$S$_4$ in the NiCo$_2$O$_4@$NiCo$_2$S$_4$ sample.

The morphology of the products obtained at different stages is observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM image (Figure S2) of the precursor at low magnification shows that a layer of precursor is evenly covered on the surface of Ni foam. A SEM image of the precursor at higher magnification is shown in Figure 3a, and many nanowires with uniform size can be seen. A TEM image of the precursor is shown in Figure 3b. The nanowire is solid and its surface is smooth. Figure 3c shows the SEM image of the NiCo$_2$O$_4$ obtained by calcining the precursor under ambient atmosphere. The nanowire morphology of the precursor is retained after calcination. However, the TEM image of the NiCo$_2$O$_4$ nanowire shown in Figure 3d reveals a porous structure. The formation of the porous structure can be ascribed to the volume shrink and the release of gaseous species during the decomposition of the precursor.

Figure 4a,b shows the typical SEM images of the NiCo$_2$O$_4@$NiCo$_2$S$_4$ nanocomposite at different magnifications. The NiCo$_2$O$_4@$NiCo$_2$S$_4$ nanocomposite shows a hierarchical structure in which NiCo$_2$S$_4$ nanosheets are attached on NiCo$_2$O$_4$ nanowires. The TEM image of the NiCo$_2$O$_4@$NiCo$_2$S$_4$ nanocomposite in Figure 4c further illustrates the hierarchical structure. A high-resolution transmission electron microscopy (HRTEM) image of the outer nanosheet is shown in Figure 4d. The interplanar spacing of the lattice fringes is about 0.23 nm, which corresponds to the (400) lattice plane of NiCo$_2$S$_4$.

The chemical states of the component elements in NiCo$_2$O$_4@$NiCo$_2$S$_4$ nanocomposite are assessed by X-ray photoelectron spectroscopy (XPS) technique. The peaks at 169.7, 529.5, 781.5, and 855.7 eV in the XPS survey spectrum (Figure S3) correspond to S 2p, O 1s, Co 2p, and Ni 2p, respectively, which indicates the presence of S, O, Co, and Ni elements in the sample. Figure 5 shows the high-resolution XPS spectrum of Ni, Co, O, and S elements. These peaks were fitted by using Gaussian fitting method. The Ni 2p XPS spectrum shown in Figure 5a contains Ni 2p$_{3/2}$, Ni 2p$_{1/2}$, and two shake-up satellite peaks. Both Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ peaks are fitted into two peaks. The peaks at 856.4 and 874.3 eV belong to Ni$^{2+}$, whereas the peaks at 855.4 and 872.9 eV belong to Ni$^{3+}$. This result suggests the coexistence of both Ni$^{2+}$ and Ni$^{3+}$ in the sample. Figure 5b shows the Co 2p XPS spectrum. Similar to the Ni element, the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ peaks are fitted into peaks corresponding to Co$^{2+}$ and Co$^{3+}$, revealing the coexistence of both Co$^{2+}$ and Co$^{3+}$ in the sample. The O 1s XPS spectrum is shown in Figure 5c. The peak at 529.2 eV is typical of metal–oxygen bonding, the peak at 531.7 eV is attributed to hydroxyl that come from water vapor in the air, and the peak at 531.7 eV is attributed to oxygen in the low-valence state. As compared to the O 1s XPS spectrum of NiCo$_2$O$_4$ nanowires (Figure S4), the peak at 529.2 eV is much weaker. This can be explained by the fact that in the NiCo$_2$O$_4@$NiCo$_2$S$_4$ nanocomposite, the NiCo$_2$O$_4$ are encapsulated by NiCo$_2$S$_4$. Figure 5d shows the S 2p XPS spectrum, which contains a main peak and a satellite peak. The main peak at 162.7 eV can be attributed to the sulfur ions that bonded with metal ions.

The specific surface area and pore size distribution of the NiCo$_2$O$_4@$NiCo$_2$S$_4$ nanocomposite are measured by N$_2$
adsorption–desorption isotherms, as shown in Figure 6a. The isotherm with significant hysteresis loops can be attributed to type IV isotherms. The Brunauer–Emmett–Teller (BET) surface area of the NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite is 58.849 m$^2$ g$^{-1}$, which is higher than that of the NiCo$_2$O$_4$ nanowires (53.892 m$^2$ g$^{-1}$, Figure S5). The higher specific surface area of the NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite can be attributed to the existence of thin NiCo$_2$S$_4$ nanosheets in the NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite. Figure 6b shows the pore size distribution of the NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite calculated by the Barrett–Joyner–Halenda (BJH) method. The pore diameter is mainly around 8 nm. The above results confirm the porous nature of the NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite. When the NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite was applied as the electrode material for supercapacitors, the porous

Figure 3. (a, b) SEM and TEM images of the precursor and (c, d) SEM and TEM images of the NiCo$_2$O$_4$ nanowires.

Figure 4. (a, b) SEM, (c) TEM, and (d) HRTEM images of the NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite.
structure can provide a large surface area for faradic redox reactions, and the pore size is suitable for ion transportation.

The unique vapor-phase hydrothermal process in the second step is crucial for the formation of the hierarchical structure of NiCo2O4@NiCo2S4 nanocomposite. If the NiCo2O4 nanowires were immersed in the thioacetamide solution in the second step, only NiCo2S4 nanotubes can be obtained (Figure S6). To understand the formation mechanism of the hierarchical structure of the NiCo2O4@NiCo2S4 nanocomposite, a series of time-dependent experiments were done. Figure 7 shows the SEM images of the products obtained by treating NiCo2O4 nanowires in the atmosphere of thioacetamide solution under hydrothermal condition at 120 °C for different periods of time. After treating for only an hour, no noticeable change can be seen, as shown in Figure 7a. This is possibly due to the slow temperature rise of the autoclave. When the reaction time reaches 2 h, some nanosheets start to evolve on the surface of NiCo2O4 nanowires, as indicated from Figure 7b. With the reaction time further prolonging, the nanosheets grow larger (Figure 7c). After 6 h, the NiCo2O4@NiCo2S4 nanocomposite with an obvious hierarchical structure can be obtained (Figure 7d). According to the above results, we believe that the reaction between NiCo2O4 and H2S in the atmosphere of thioacetamide solution is slower than that in the solution. During the reacting process, the outer layer of the NiCo2O4 nanowires is gradually converted to NiCo2S4 nanosheets. Finally, the NiCo2O4@NiCo2S4 nanocomposite with a hierarchical structure is obtained.

The NiCo2O4@NiCo2S4 nanocomposite is applied as an electrode material for supercapacitors. The electrochemical performances are evaluated by cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) methods. Figure 8a shows a series of CV curves of the NiCo2O4@NiCo2S4 electrode measured in a three-electrode cell with the scan rates in the range of 10−100 mV s−1. All of the CV curves show significant redox peaks, indicating the pseudocapacitive characteristics of the NiCo2O4@NiCo2S4 active material. As the scan rate increases, the magnitude of the current response increases, and the anodic and cathodic peaks shifts to more a positive and negative potential, respectively. The GCD curves

Figure 5. XPS spectra of the NiCo2O4@NiCo2S4 nanocomposite: (a) Ni 2p, (b) Co 2p, (c) O 1s, and (d) S 2p.

Figure 6. (a) N2 adsorption and desorption isotherms of the NiCo2O4@NiCo2S4 nanocomposite. (b) BJH pore size distribution curve.
The GCD curves appear as obvious platforms during the charging and discharging process, which can be attributed to the redox reactions occurring in the process of charging and discharging. The IR drop in the GCD curves can be attributed to the internal resistance of the electrode. The capacitances of the electrode can be calculated by using the following equations.  

\[
C_s = \frac{I \times \Delta t}{m \times \Delta V}
\]

where \( C_s \) (F g\(^{-1}\)) is the specific capacitance, \( I \) (A) is the current during the discharge process, \( \Delta t \) (s) is the discharge time, \( \Delta V \) (V) is the potential window, and \( m \) (g) is the mass of the active materials. When the current densities are 1, 2, 4, 6, 8, and 10 A g\(^{-1}\), the specific capacities are 1872, 1808, 1720, 1632, 1456, and 1320 F g\(^{-1}\), respectively. With increase in the current density from 1 to 10 A g\(^{-1}\), the capacitance retention of the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\) electrode is about 70.5%, suggesting a good rate capability.

Figure 8c shows the comparative GCD curves of the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\) electrode and the NiCo\(_2\)O\(_4\) electrode at a current density of 1 A g\(^{-1}\). It is obvious that the discharging time of the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\) electrode is much longer than that of the NiCo\(_2\)O\(_4\) electrode. The specific capacitance of the NiCo\(_2\)O\(_4\) electrode is only 722 F g\(^{-1}\) at 1 A g\(^{-1}\).

Cycling stability of the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\) electrode was tested at a current density of 5 A g\(^{-1}\) for 4000 GCD cycles, and the results are displayed in Figure 8d. With the increase in cycles, the capacitance slowly deteriorates. After 4000 cycles, a capacitance retention of about 65% is achieved. The deterioration of capacitance during the cycling process can be attributed to the oxidation of NiCo\(_2\)S\(_4\) in alkaline electrolytes.

The electrochemical impedance spectra of the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\) and NiCo\(_2\)O\(_4\) electrodes were tested in a frequency range of 100 kHz to 0.01 Hz with an amplitude of 5 mV. The Nyquist plots are shown in Figure 8e. All of the plots contain a negligible semicircle in the high-frequency region and a straight line in the low-frequency region. The semicircle reflects the charge-transfer resistance in the electrode–electrolyte interface. The negligible semicircle in the plots indicates that the charge-transfer resistance of the two electrodes is very low. This result can be attributed to the direct growth of the electrode materials on the Ni foam. The sloping straight line in the low-frequency region reflects the Warburg impedance. The slope of the lines reveals the diffusion rates of the electrolyte ions into the electrode materials.

To evaluate the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\) electrode for practical application, a hybrid supercapacitor device was assembled by using the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\) nanocomposite as the positive electrode material, activated carbon (AC) as the negative electrode material, and a 3 mol L\(^{-1}\) KOH aqueous solution as the electrolyte. As indicated from the CV curves of the positive and negative electrode materials measured in the three-electrode cell (Figure 9a), the working potential windows of the positive and negative electrode materials are in different regions. Therefore, the working potential window of the hybrid supercapacitor can be extended because of the complementary working potential windows of the positive and negative electrode materials. Figure 9b displays a series of CV curves of the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\)/AC hybrid supercapacitor in a potential range of 0–1.6 V at the scan rates of 10, 20, 40, 60, 80, and 100 mV s\(^{-1}\). With the increase in the scan rate, the CV curves retain the similar shape, indicating that the hybrid supercapacitor could stably work in such a wide potential window. Figure 9c displays the GCD curves of the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\)/AC hybrid supercapacitor at the current densities
from 2 to 10 A g\(^{-1}\). The shape of the charge and discharge curves is nonlinear due to the occurrence of faradic redox reactions. The specific capacitances of the hybrid supercapacitor are 114, 83, 64, 50, and 46 F g\(^{-1}\) at the current densities of 2, 4, 6, 8, and 10 A g\(^{-1}\). The cycling stability of the device was measured at the current density of 4 A g\(^{-1}\) for 2000 GCD cycles (Figure 9d). The specific capacitance reaches a maximum of 131 F g\(^{-1}\) after 200 cycles, and then slowly decreases. After 2000 cycles, the specific capacitance of the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\)//AC device is 103 F g\(^{-1}\), which is about 78% of the maximum value. The energy density (\(E\)) and the power density (\(P\)) of the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\)//AC device can be calculated according to the following equations.\(^{44}\)

\[
E = \frac{1}{2}C_\Delta V^2
\]

(2)

\[
P = \frac{E}{\Delta t}
\]

(3)

Figure 9e shows the Ragone plot of the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\)//AC device. At a current density of 2 A g\(^{-1}\), the energy density and the power density of the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\)//AC device are 35.6 W h kg\(^{-1}\) and 1.5 kW kg\(^{-1}\), respectively. At the current density of 10 A g\(^{-1}\), the energy density and the power density of the device are 14.4 W h kg\(^{-1}\) and 7.5 kW kg\(^{-1}\), respectively. Finally, a light-emitting diode (LED) is successfully illumined by two series connected NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\)//AC devices (Figure 9f), which further proves the possibility of the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\) nanocomposite for practical charge storage applications.

■ CONCLUSIONS

In conclusion, the NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\) nanocomposite with a hierarchical structure was prepared by a multistep process. The vapor-phase hydrothermal process in the second step is crucial for the formation of NiCo\(_2\)S\(_4\) nanosheets on the surface of NiCo\(_2\)O\(_4\) porous nanowires. The hierarchical NiCo\(_2\)O\(_4@\)NiCo\(_2\)S\(_4\) nanocomposite is an excellent candidate for electrochemical energy storage applications.
NiCo$_2$S$_4$ nanocomposite has excellent structural advantages such as large specific surface areas and short diffusion pathways for electrolyte ions. When acting as an electrode material for supercapacitor, the NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite shows much enhanced supercapacitor performances than that of the NiCo$_2$O$_4$ porous nanowires. The experimental results indicate that the hierarchical NiCo$_2$O$_4$@NiCo$_2$S$_4$ nanocomposite is suitable for high-performance supercapacitor applications.

**EXPERIMENTAL SECTION**

All of the chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. The purity of these chemical reagents was of analytical grade.

**Synthesis of NiCo$_2$O$_4$ Nanowires Array on Ni Foam.** A piece of Ni foam with a size of 2 cm × 2 cm was washed with 3 mol L$^{-1}$ hydrochloric acid, acetone, ethanol, and deionized water in sequence. Ni(NO$_3$)$_2$·6H$_2$O (0.291 g, 1 mmol), Co(NO$_3$)$_2$·6H$_2$O (0.582 g, 2 mmol), and CO(NH$_2$)$_2$ (0.420 g, 7 mmol) were together dissolved in 40 mL deionized water in a beaker. The solution was transferred into a stainless-steel autoclave with a Teflon liner of 60 mL capacity, and the Ni foam was immersed in the solution. After that, the autoclave was sealed and heated at 120 °C for 6 h. The precursor-loaded Ni foam was fully washed with deionized water, dried under vacuum at 50 °C for 2 h, and then calcined in an ambient atmosphere at 380 °C for 2 h.

**Synthesis of NiCo$_2$O$_4$@NiCo$_2$S$_4$ Nanocomposite on Ni Foam.** Thioacetamide (0.380 g, 5 mmol) was dissolved in 25 mL deionized water in a beaker. Then, the solution was transferred into a 60 mL Teflon-lined stainless-steel autoclave. The NiCo$_2$O$_4$/Ni foam was placed on a Teflon support above the solution. After that, the autoclave was sealed and heated at 120 °C for 6 h. The NiCo$_2$O$_4$@NiCo$_2$S$_4$/Ni foam was washed with deionized water and ethanol in sequence, and then dried under vacuum at 50 °C for 2 h. The mass loading of NiCo$_2$O$_4$@NiCo$_2$S$_4$ on Ni foam is about 2.0 mg cm$^{-2}$.

![Figure 9](image-url)
Characterizations. The composition of the samples was determined by X-ray powder diffraction (XRD, Bruker D8 Advance, Cu Kα radiation), X-ray photoelectron spectroscopy (XPS, ESCALab MKII, Al Kα radiation), and energy-dispersive X-ray spectra. The morphology of the samples was observed by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, Hitachi HT-7700). The surface area of the sample was measured by N₂ adsorption/desorption (Micromeritics ASAP 2020M) at 77 K. The electrochemical performances were measured on a CHI-660D electrochemical workstation (Chenhua Corp., Shanghai, China).

Electrochemical Measurements. The electrochemical performances were tested in a three-electrode cell. The working electrode was the NiCo₂O₄/Ni foam or NiCo₂O₄@NiCo₂S₄/Ni foam, the counter electrode was a platinum plate, and the reference electrode was an Hg/HgO electrode. The electrolyte was a 3 mol L⁻¹ KOH aqueous solution.

The hybrid supercapacitor device was assembled by using NiCo₂O₄@NiCo₂S₄/ Ni foam as the positive electrode, activated carbon/Ni foam as the negative electrode, and cellulose paper as the separator. The activated carbon was prepared according to literature report. A 3 mol L⁻¹ KOH aqueous solution, which was soaked in the separator, served as the electrolyte. The electrode and separator were packed in a CR2032 battery case.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00742.

XRD patterns of the precursor and NiCo₂O₄, SEM image of the precursor at low magnification, XPS survey spectrum of the NiCo₂O₄@NiCo₂S₄ nanocomposite, Ni 2p, Co 2p, and O 1s XPS spectra of NiCo₂O₄ nanowires, Ni₄ adsorption and desorption isotherms of the NiCo₂O₄ nanowires, and TEM image of the NiCo₂S₄ nanotube (PDF).

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: zhwang@ahnu.edu.cn.

ORCID
Zhenghua Wang: 0000-0002-1073-8055

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (No. 21671007) is gratefully acknowledged.

■ REFERENCES

(1) Conway, B. E.; Birss, V.; Wojtowicz, J. The role and utilization of pseudocapacitance for energy storage by supercapacitors. J. Power Sources 1997, 66, 1–14.
(2) Aričić, A. S.; Bruce, P.; Scrosati, B.; Tarascon, J. M.; Van Schalkwijk, W. Nanostructured materials for advanced energy conversion and storage devices. Nat. Mater. 2005, 4, 366–377.
(3) Simon, P.; Gogotsi, Y. Materials for electrochemical capacitors. Nat. Mater. 2008, 7, 845–854.
(4) Liu, C.; Li, F.; Ma, L. P.; Cheng, H. M. Advanced Materials for Energy Storage. Adv. Mater. 2010, 22, E82–E62.
(5) Zhai, Y.; Dou, Y.; Zhao, D.; Fulvio, P. F.; Mayes, R. T.; Dai, S. Carbon Materials for Chemical Capacitive Energy Storage. Adv. Mater. 2011, 23, 4828–4850.
(6) Jiang, J.; Li, Y.; Liu, J.; Huang, X.; Yuan, C.; Lou, X. W. Recent Advances in Metal Oxide-based Electrode Architecture Design for Electrochemical Energy Storage. Adv. Mater. 2012, 24, 5166–5180.
(7) Wang, G.; Zhang, L.; Zhang, J. A review of electrode materials for electrochemical supercapacitors. Chem. Soc. Rev. 2012, 41, 797–828.
(8) Wu, Z.; Zhang, X. B. Design and Preparation of Electrode Materials for Supercapacitors with High Specific Capacitance. Acta Phys.-Chim. Sin. 2017, 33, 305–313.
(9) Gao, Y. P.; Huang, K. J. NiCo₃S₄ Materials for Supercapacitor Applications. Chem. Asian J. 2017, 12, 1969–1984.
(10) Guan, B. Y.; Yu, L.; Wang, X.; Song, S.; Lou, X. W. Formation of Onion-Like NiCo₃S₄ Particles via Sequential Ion-Exchange for Hybrid Supercapacitors. Adv. Mater. 2017, 29, No. 1605051.
(11) Liu, Y.; Yang, Z.; Zhong, Y.; Tade, M.; Zhou, W.; Shao, Z. Molecular Design of Mesoporous NiCo₂O₄ and NiCo₂S₄ with Sub-Micrometer-Polyhedron Architectures for Efficient Pseudocapacitive Energy Storage. Adv. Funct. Mater. 2017, 27, No. 1701229.
(12) Wei, C.; Huang, Y.; Xue, S.; Zhang, X.; Chen, X.; Yan, J.; Yao, W. One-step hydrothermal synthesis of flaky attached hollow-sphere structure NiCo₂S₄ for electrochemical capacitor application. Chem. Eng. J. 2017, 317, 873–881.
(13) Wen, Y.; Peng, S.; Wang, Z.; Hao, J.; Qin, T.; Lu, S.; Zhang, J.; He, D.; Fan, X.; Cao, G. Facile synthesis of ultrathin NiCo₂S₄ nanoneedles grown on mesocarbon microbeads with synergistic electrochemical properties as electrodes for symmetric supercapacitors. J. Mater. Chem. A 2017, 5, 7144–7152.
(14) Guan, C.; Liu, X.; Ren, W.; Li, X.; Cheng, C.; Wang, J. Rational Design of Metal-Organic Framework Derived Hollow NiCo₂O₄ Arrays for Flexible Supercapacitor and Electrocatalysis. Adv. Energy Mater. 2017, 7, No. 1602391.
(15) Yuan, Y.; Wang, W.; Yang, J.; Tang, H.; Ye, Z.; Zeng, Y.; Lu, J. Three-Dimensional NiCo₂O₄@MnMoO₄ Core-Shell Nanoarrays for High-Performance Asymmetric Supercapacitors. Langmuir 2017, 33, 10446–10454.
(16) Zhang, Y.; Zhang, Y.; Zhang, D.; Sun, L. Urchin-like NiCo₂O₄ nanoneedles grown on mesocarbon microbeads with synergistic electrochemical properties as electrodes for symmetric supercapacitors. Dalton Trans. 2017, 46, 9457–9465.
(17) Ma, F. X.; Yu, L.; Xu, C. Y.; Lou, X. W. Self-supported formation of hierarchical NiCo₂O₄ tetragonal microtubes with enhanced electrochemical properties. Energy Environ. Sci. 2016, 9, 862–866.
(18) Zhang, P.; Guan, B. Y.; Yu, L.; Lou, X. W. Formation of Double-Shelled Zinc-Cobalt Sulphide Dodecahedral Cages from Bimetallic Zeolitic Imidazolate Frameworks for Hybrid Supercapacitors. Angew. Chem., Int. Ed. 2017, 56, 7141–7145.
(19) Deng, S. J.; Zhong, Y.; Zeng, Y. X.; Wang, Y. D.; Wang, X. L.; Lu, X. H.; Xia, X. H.; Tu, J. P. Hollow TiO₂@Co₃O₄ Core–Branch Arrays as Bifunctional Electrocatalysts for Efficient Oxygen/Hydrogen Production. Adv. Sci. 2018, 5, No. 1700772.
(20) Kuang, M.; Wen, Z. Q.; Guo, X. L.; Zhang, S. M.; Zhang, Y. X. Engineering firecracker-like beta-manganese dioxide@spinel nickel cobaltates nanostuctures for high-performance supercapacitors. J. Power Sources 2014, 270, 426–433.
(21) Chen, W.; Xia, C.; Alshareef, H. N. One-Step Electrodeposited Nickel Cobalt Sulphide Nanostructure Arrays for High-Performance Asymmetric Supercapacitors. ACS Nano 2014, 8, 9531–9541.
(22) Han, X.; Tao, K.; Wang, D.; Han, L. Design of a porous cobalt sulphide nanosheet array on Ni foam from zeolitic imidazolate frameworks as an advanced electrode for supercapacitors. Nanoscale 2018, 10, 2735–2741.
(23) Paravannoor, A.; Ranjusha, R.; Asha, A. M.; Vani, B. J.; Kalluri, S.; Subramanian, K. R. V.; Sivakumar, N.; Kim, T. N.; Nair, S. V.; Balakrishnan, A. Chemical and structural stability of porous thin film NiO nanowire based electrodes for supercapacitors. Chem. Eng. J. 2013, 220, 360–366.
Hierarchically porous Co$_9$O$_7$/C nanowire arrays derived from a metal-organic framework for high performance supercapacitors and the oxygen evolution reaction. *J. Mater. Chem. A* 2016, 4, 16516−16523.

Mai, L. Q.; Yang, F.; Zhao, Y. L.; Xu, X.; Xu, L.; Luo, Y. Z. Hierarchical MnMoO$_4$/CoMoO$_4$ heterostructured nanowires with enhanced supercapacitor performance. *Nat. Commun.* 2011, 2, 1181.

Yu, L.; Zhang, G.; Yuan, C.; Lou, X. W. Hierarchical NiCo$_2$O$_4$@MnO$_2$ core-shell heterostructured nanowire arrays on Ni foam as high-performance supercapacitor electrodes. *Chem. Commun.* 2013, 49, 137−139.

Hou, J.; Cao, C.; Idrees, F.; Ma, X. Hierarchical Porous Nitrogen-Doped Carbon Nanosheets Derived from Silk for Ultrahigh-Capacity Battery Anodes and Supercapacitors. *ACS Nano* 2015, 9, 2556−2564.

Chen, F.; Wan, P.; Xu, H.; Sun, X. Flexible Transparent Supercapacitors Based on Hierarchical Nanocomposite Films. *ACS Appl. Mater. Interfaces* 2017, 9, 17865−17871.

Liu, F. F.; Zhou, J. J.; Li, G. C.; Wu, M. K.; Tao, K.; Yi, F. Y.; Zhao, W. N.; Han, L. A hierarchical NiO/NiMn-layered double hydroxide nanosheet array on Ni foam for high performance supercapacitors. *Dalton Trans.* 2017, 46, 7388−7391.

Yan, J.; Wang, Q.; Wei, T.; Fan, Z. Recent Advances in Design and Fabrication of Electrochemical Supercapacitors with High Energy Densities. *Adv. Energy Mater.* 2014, 4, No. 130816.

Lim, E.; Kim, H.; Jo, C.; Chun, J.; Ku, K.; Kim, S.; Lee, H. I.; Nam, I. S.; Yoon, S.; Kang, K.; Lee, J. Advanced Hybrid Supercapacitor Based on a Mesoporous Niobium Pentoxide/Carbon as High-Performance Anode. *ACS Nano* 2014, 8, 8968−8978.

Chen, Y. M.; Li, Z.; Lou, X. W. General Formation of M$_x$Co$_3$S$_4$ (M = Ni, Mn, Zn) Hollow Tubular Structures for Hybrid Supercapacitors. *Angew. Chem., Int. Ed.* 2015, 54, 10521−10524.

Li, B.; Dai, F.; Xiao, Q.; Yang, L.; Shen, J.; Zhang, C.; Cai, M. Nitrogen-doped activated carbon for a high energy hybrid supercapacitor. *Energy Environ. Sci.* 2016, 9, 102−106.

Ruan, Y.; Lv, L.; Li, Z.; Wang, C.; Jiang, J. Ni nanoparticles@Ni-Mo nitride nanorod arrays: a novel 3D-network hierarchical structure for high areal capacitance hybrid supercapacitors. *Nanoscale* 2017, 9, 18032−18041.

Sankar, K. V.; Lee, S. C.; Seo, Y.; Ray, C.; Liu, S.; Kundu, A.; Jun, S. C. Binder-free cobalt phosphate one-dimensional nanograssess as ultrahigh-performance cathode material for hybrid supercapacitor applications. *J. Power Sources* 2018, 373, 211−219.

Wang, Z.; He, B.; Kong, W.; Lu, C. Synthesis of NiCo$_2$S$_4$ Nanocages as Pseudocapacitor Electrode Materials. *ChemistrySelect* 2016, 1, 4082−4086.

Choudhury, T.; Saied, S. O.; Sullivan, J. L.; Abbot, A. M. Reduction of oxides of iron, cobalt, titanium and niobium by low-energy ion bombardment. *J. Phys. D: Appl. Phys.* 1989, 22, 1185.

Jiménez, V. M.; Fernández, A.; Espinós, J. P.; González-Elpe, A. R. The state of the oxygen at the surface of polycrystalline cobalt oxide. *J. Electron Spectrosc. Relat. Phenom.* 1995, 71, 61−71.

Roginskaya, Y. E.; Morozova, O. V.; Lubnin, E. N.; Ultina, Y. E.; Lopukhova, G. V.; Trasatti, S. Characterization of Bulk and Surface Composition of CoxNi-xOy Mixed Oxides for Electrocatlysis. *Langmuir* 1997, 13, 4621−4627.

Wang, X.; Xiao, Y.; Su, D.; Zhou, L.; Wu, S.; Han, L.; Fang, S.; Cao, S. High-quality Porous Cobalt Monoxide Nanowires @ Ultrathin Manganese dioxide Sheets Core-Shell Nanowire Arrays on Ni Foam for High-Performance Supercapacitor. *Electrochim. Acta* 2016, 194, 377−384.

He, G.; Qiao, M.; Li, W.; Lu, Y.; Zhao, T.; Zou, R.; Li, B.; Darr, J. A.; Hu, J.; Titirici, M. M.; Parkin, I. P. S. N-Co-Doped Graphene-Nickel Cobalt Sulphide Aerogel: Improved Energy Storage and Electrocatlytic Performance. *Adv. Sci.* 2017, 4, No. 1600214.

Qu, D. Y.; Shi, H. Studies of activated carbons used in double-layer capacitors. *J. Power Sources* 1998, 74, 99−107.