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Hierarchical nickel nanowire@NiCo₂S₄ nanowhiskers composite arrays with test-tube-brush-like structure for high-performance supercapacitors

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Well-ordered, hierarchical and nanostructured composite electrodes have gained tremendous research attentions for energy storage applications, because of their highly efficient electron and ion transport channels and abundant electrochemically active sites. However, it still remains a great challenge to prepare such architectures in large scale with high active material mass loadings for making better use of the whole electrode area. Herein, needle-like NiCo₂S₄ nanowhiskers are radially grown on a uniform nickel nanowire array (NNA), forming a unique densely-packed test-tubebrush-like nanostructure. Since these NiCo₂S₄ nanowhiskers are intrinsically highly electrically conductive, the hierarchical electrode structure can drastically elevate the charge transport ability in the whole electrode region; additionally, it can greatly help to release stresses at micro- and nano-scales, leading to robust mechanical flexibility and superior energy storage capability. Experimental results show that this composite array electrode exhibits an ultrahigh specific capacitance of 1,523 F g⁻¹ at a mass loading of 4.03 mg cm⁻² at the current density of 1 A g⁻¹, and a rate capability of 61.8% from 1 to 40 A g⁻¹, together with a superior cycle stability of 92.4% of capacitance retention after 20,000 cycles at a current density as high as 10 A g⁻¹. An asymmetric supercapacitor consisting of NNA@NiCo₂S₄ (NNANCS) cathode and activated carbon (AC) anode delivers a maximum energy density of 47.29 W h kg⁻¹ at the power density of 793.5 W kg⁻¹ and still an energy density of 29.50 W h kg⁻¹ at a maximum power density of 27.64 kW kg⁻¹. This work may inspire new ideas of constructing high-performace electrodes for energy storage.

Introduction

The last few decades have witnessed the soaring growth of electrochemical energy storage technology.¹⁻³ Among all available energy storage devices, supercapacitors have attracted tremendous attentions for their high power density, short charging time, and long cycle life.⁴⁻⁷ However, their practical applications have been largely limited due to their low energy density, especially for electrochemical double-layer capacitors (EDLCs) where carbon based materials are generally used as electrodes.⁸⁻¹⁰ The introduction of pseudocapacitive materials such as transition metal oxides/hydroxides and conducting polymers as supercapacitor electrodes can significantly increase the energy density,¹¹⁻¹⁴ but most

capability and greatly compromised cycle life due to the intrinsically low electronic conductivity and structural instability during redox reactions after repeated charging and discharging.¹⁵⁻¹⁸ Therefore, it is challenging and critically important to enhance the energy density of pseudocapacitive supercapacitors without sacrificing their rate capability and cycle life.

pseudocapacitive electrode materials suffer from inferior rate

The performance of pseudocapacitive electrode materials is highly dependent on the transport ability of both electrons and ions.¹⁹ Since most of them are wide band-gap semiconductors or insulators,¹⁵ it is highly desirable to improve the electronic conductivity for better electrochemical performance.²⁰⁻²² One conventional approach is to mix pseudocapacitive material powders with conductive agent and polymer binder to prepare thin-film electrodes, 23-27 but it inevitably increases contact resistance.^{21,28} Recently, reticular conductive backbones such as nickel foam and carbon clothes were introduced as substrates to prepare free-standing electrodes for higher specific surface areas and excellent electronic conductivity.^{9,22,29} But these conductive backbones are still far from satisfactory due to their limited specific surface area and the random geometry.^{30,31} Recently, nanostructured carbon based electrode scaffolds have been for intensively studied as conductive frameworks

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pseudocapacitive active materials,⁸ but the weak interaction between the inorganic species and carbon based materials (such as graphene and carbon nanotube) usually leads to nonuniform deposition of the inorganic component on the surface of backbones.³² As compared, nanostructured metallic conductive skeletons such as nickel nanowires and silver nanowires have attracted tremendous interests due to the intrinsically hydrophilic nature, excellent ohmic conductance, and superior mechanical properties.^{33,34} But challenges are still huge in distributing active materials uniformly with a high mass loading, by which we can make use of the electrode spaces as much as possible.³⁵ With all these considerations, it is highly desirable to develop a general method that can be applied to prepare a wide range of pseudocapacitive electrodes.

A general strategy to increase the electrode active mass loading is to develop porous conductive scaffold with sufficiently high packing density of active mass to maximize space utilization.³⁶ Inspired by the interesting geometric structure of test-tube-brush, we propose a well-ordered, hierarchical, nanostructured and densely packed test-tubebrush-like composite electrode with needle-like active materials radially grafted on nickel nanowires. This electrode shows a unique hierarchical structure; it can not only maximize the utilization of the electrode space and achieve a high mass loading, but also provide regular channels and rich active redox sites. In addition, since each of the "test-tube-brush" would not intertwine with each other, the structural stability can be highly maintained during charging/discharging and being bended. Here, we choose NiCo₂S₄ nanowhiskers as the active materials for model study, due to the following reasons: 1) NiCo₂S₄ has ultrahigh electronic conductivity (about 2 orders of magnitude higher than that of either Ni_xS_v or Co_xS_v).^{17,37,38} 2) This bimetal sulfide has a high specific capacitance owing to the electrochemical contributions from both nickel ions and cobalt ions. $^{\rm 39}$ 3) Furthermore, since the morphology of nickel cobalt (carbonate) hydroxide can be conveniently controlled through solvothermal reaction and NiCo₂S₄ can be reconstructed from nickel cobalt (carbonate) hydroxide (e.g. $NiCo_2(CO_3)_{1.5}(OH)_3$) through anion exchange reactions by Kirkendall effects,⁴⁰ the morphology of NiCo₂S₄ can also be modulated, which makes it much easier to modulate the composite electrode architecture.

Here in this work, the test-tube-brush-like nickel nanowire@NiCo $_2S_4$ (NNANCS) composite electrode material was synthesized by growing NiCo₂S₄ nanowhiskers on nickel nanowires via a two-step hydrothermal method. By rationally controlling the growth kinetics of NiCo2S4, the composite electrode exhibits a unique test-tube-brush-like structure, rendering abundant electrochemically active sites exposed to the electrolyte and is able to release strain and shorten the transport distance of ions, which is of great importance for further exploiting the active materials. As a result, the integrated NNANCS electrode exhibits greatly enhanced specific capacitance and rate capability even at a high mass loading. It also shows excellent cycling stability. An asymmetric supercapacitor employing NNANCS as positive electrode and activated carbon (AC) as negative electrode can deliver a high

energy density and a high power density. This technology holds great promise for future high performance energy storage device applications.

Experimental

All chemicals are acquired from Alfa Aesar and directly used without further purification. The nickel nanowire arrays (NNA) is prepared in an optimized condition following our previous work,³³ and the fabrication of NNANCS was synthesized through a two-step hydrothermal method. The detailed synthesis process is as follows.

Preparation of NNA

The NNA is prepared in a modified method. Firstly, a thin layer of Pd active layer was deposited on a piece of commercial Ti foil (40 μm in thickness) through chemical bath plating, during which the Ti foil was immersed in a 50 mL solution containing 15 mM PdCl₂, 0.3 vol% HCl, 30 vol% ammonia solution and 5mM hydrazine and kept at 60 °C for 30 minutes. Then the Ti-Pd foil was washed with deionized water and ethanol, and dried in air at 50 °C for 5 hours. After that, a 50 mL aqueous solution (containing 0.10 M Ni(Ac)₂, 37.5 mM $Na_3C_6H_5O_7$ and 0.20 mM H₂PtCl₆, denoted as solution A) and another 50 mL aqueous solution (containing 8.5 vol% of hydrazine, denoted as solution B) were prepared. Subsequently, the pH values of both solutions were adjusted to 12.5 with 6 M KOH aqueous solution at room temperature measured by a pH meter (HORIBA, F-71). Then the solution A and solution B were heated to 80 °C and mixed, and placed in a uniform magnetic field (intensity: 100 mGs, generated by a Helmholtz coil (PEM-50, Litian Magnetoelectrical Science & Technology Co., Ltd)). The Ti-Pd foil was immersed in the mixed solution, with its face vertical to the direction of the magnetic field. After 60 minutes of reaction at 80 °C, nickel nanowire arrays were eventually vertically grown on the Pd layer.

Fabrication of the NNANCS composite electrode

The preparation of NNANCS follows a two-step hydrothermal method. Typically, 2.48 mg Co(NO₃)₂·6H₂O, 1.24 mg Ni(NO₃)₂·6H₂O and 0.90 mg urea were dissolved in 60 mL solvent (consisting of 20 mL water, 20 mL ethanol and 20 mL glycol) to form a transparent pink solution followed by immersing a piece of NNA $(2 \times 2 \text{ cm}^2)$ into the solution. This solution immersed with NNA was then transferred to a 100 mL Teflon-lined stainless steel autoclave and aged at 120 °C for 10 hours. The morphology and mass loading of the nickel cobalt carbonate hydroxide precursors grown on NNA was controlled by simply changing the concentration of the solution during the first hydrothermal process. Detailed data of the concentrations of the solutions are presented in Table S1. After the first hydrothermal step, NNA coated with nickel cobalt carbonate hydroxide precursor was taken out and rinsed with ethanol and deionized water for several times and then dried at 60 °C for 12 hours.

In the second step of the hydrothermal reaction, the NNA@precursor samples were immersed in an aqueous solution containing 0.01 M thioacetamide (TAA) and

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transferred to a 100 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 5h. Later on, the samples were taken out and rinsed with ethanol and deionized water for several times, followed by drying process at 60 °C for 12 hours. Fabrication of NiCo₂S₄//AC asymmetric supercapacitor (ASC)

The NiCo₂S₄//AC ASC was assembled by using NNA@ NiCo₂S₄ as the positive electrode and activated carbon (AC) as the negative electrode. The negative electrode was prepared by mixing activated carbon, acetylene black and polyvinylidene fluoride with a mass ratio of 7:2:1 in N-Methyl pyrrolidone and then plated on Ti foil.

The masses of the positive and negative electrodes were balanced according to the equation below:

$$\frac{m_+}{m_-} = \frac{C_{\rm s} \pm \Delta V_-}{C_{\rm s} \pm \Delta V_+} \tag{1}$$

where m_{+} and m_{-} are the masses of the cathode and the anode, respectively; C_{s+} and C_{s-} are the specific capacitances of the cathode and the anode, respectively; ΔV_{+} and ΔV_{-} are the voltage ranges of the cathode and the anode, respectively. Material characterizations

Material characterizations

The crystal structure of the samples was characterized by X-ray powder diffraction patterns (XRD, Rint-2000V/PC, Rigaku, Japan). The morphology was studied by Field-emission Scanning Electron Microscopy (FE-SEM, Carl Zeiss, ZEISS SUPRA55). TEM results were obtained from Field-emission Transmission Electron Microscopy (FEI Tecnai G² F30). X-ray photoelectron spectroscopy was conducted on X-ray photonelectron spectrometer (XPS, Thermo Fisher, ESCALAB 250X). The textural characterizations of the samples were performed by Nitrogen adsorption at 77 K in a micromeritics ASAP 2020 apparatus, and the specific surface areas were measured via Brunauer-Emmett-Teller (BET) method.

Electrochemical measurements

The electrochemical properties of the electrodes were measured at room temperature in three-electrode configuration in 1 M KOH solution, with NNANCS as the working electrode, a Pt foil and a saturated calomel electrode as the counter electrode and the reference electrode respectively. The electrochemical measurements of devices were conducted in two-electrode configuration, with NNANCS as positive electrode and activated carbon (AC) as negative electrode.

The capacitances of the active materials were measured from cyclic voltammetry (CV) curves and galvanostatic charge/discharge (GCD) curves according to the following equations:

For GCD curves:

$$C_{\rm s} = \frac{I\Delta t}{mV} \tag{2}$$

where *I* is the current density, Δt is the discharge time, *m* is the mass of active materials, *V* is the potential range, and C_s is the specific capacitance of the electrode.

For CV curves:

$$C_{\rm s} = \frac{\int I \, dV}{2vmV} \tag{3}$$

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where *I* is the current density, *V* is the potential range, *v* is the scan rate, *m* is the mass of active materials, and C_s is the specific capacitance of the electrode.

The capacitances of the devices were calculated from galvanostatic charge/discharge curves according to the following equations:

$$C_{\rm ASC} = \frac{I\Delta t}{M\Delta V} \tag{4}$$

where *I* is the current density, Δt is the discharge time, *M* is the total mass of positive and negative materials ($M = m_+ + m_-$), *V* is the potential range, and C_{ASC} is the specific capacitance of the asymmetric supercapacitor.

The calculations of energy and power density of ASCs are based on the total weight of the two electrodes in the ASCs according to the following equations:

$$E = \frac{C_{\rm ASC} \Delta V^2}{2} \tag{5}$$

$$P = \frac{E}{\Delta t} = \frac{C_{\rm ASC} \Delta V^2}{2\Delta t} \tag{6}$$

where *E* is the energy density, *P* is the power density, C_{ASC} is the capacitance of the asymmetric supercapacitor, ΔV is the potential range, and Δt is the discharge time.

Results and discussion

Figure 1 shows the schematic preparation process of the NNANCS composite material. The NNA was synthesized in a modified method based on our previous report (see experimental section for details)³³. The composite electrode was synthesized via a two-step hydrothermal method. In the first step, nickel-cobalt carbonate hydroxides precursor is vertically grown on nickel nanowires through the reaction between nickel and cobalt cations and the hydrolysis products of urea (CO_3^{2-} and OH⁻). In the second step, the precursor is transformed into NiCo₂S₄ through an anion-exchange reaction in thioacetamide (TAA) solution. The morphology and mass loading of the composite can be conveniently controlled by adjusting the concentration of the solution during the first hydrothermal reaction.

The crystalline information of the samples can be obtained from X-ray diffraction (XRD) analysis, which is shown in Figure 2a. As can be seen, the diffraction pattern of the NNA sample is in accordance with that of pure metallic nickel, with the peaks at 44.5°, 51.8° and 76.4° corresponding to its (111), (200) and (220) planes, respectively. For the precursors grown on NNA, the set of peaks can be ascribed to Co(CO₃)_{0.5}OH (JCPDS Card No. 48-0083). This is not surprising because the partially substitution of Ni ions for Co ions only results in insignificant changes in the structure.¹⁷ Therefore, it is reasonable to deduce the formation of NiCo₂(CO₃)_{1.5}(OH)₃ in the NNA@precursor sample. For the samples prepared after

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the second hydrothermal treatment, the peaks can be well indexed to both metallic nickel and NiCo₂S₄ (JCPDS Card No. 24-0334), with the peaks at 16.3°, 26.7°, 31.5°, 38.2°, 47.7°, 50.3°, 55.0° corresponding well to the respective (111), (220), (311), (400), (422), (511), (440) planes of the cubic NiCo₂S₄. No peaks related to $Co(CO_3)_{0.5}OH$ were found, indicating that the precursor was converted to NiCo2S4 after the second hydrothermal treatment.

X-ray photoelectron spectroscopy (XPS) study was carried out to investigate the chemical composition and electronic states of the elements in the samples. The Ni 2p spectrum (Figure 2b) and the Co 2p spectrum (Figure 2c) show similar contours. By using the Gaussian fitting method, the Ni 2p_{3/2} and Ni $2p_{1/2}$ spectra can be fitted with two spin-orbit doublets that are characteristic of Ni³⁺/Ni²⁺. The peak at 853.5 eV and the peak at 871 eV correspnd to the Ni³⁺ ions; the peak located at 855.8 eV and the peak at 874.2 corresponds to Ni²⁺ ions. Similarly, the Co 2p spectrum can also be fitted with two spinorbit doublets that are characteristic of Co^{3+}/Co^{2+} . The S 2p spectrum is shown in Figure 2d, in which the peaks located at 162.1, 163.5 and 169.2 eV are attributed to S $2p_{1/2},$ S $2p_{3/2}$ and a shakeup satellite, respectively. These results show that the composite is composed of $Ni^{2+},\ Ni^{3+},\ Co^{2+},\ Co^{3+}$ and S^{-2} ions, which is in accordance with literatures for NiCo₂S₄.^{40,41}

The morphology of the as-prepared NNANCS composite was revealed by scanning electron microscope (SEM) and transmission electron microscope (TEM), which is shown in Figure 3. Figure 3a-d show the morphology of the test-tubebrush-like NNANCS at different magnifications. As can be seen, the $NiCo_2S_4$ grown on the nickel nanowire are fine nanowhiskers with an average diameter of about 20 nm and length of about 1 μ m. They are densely and uniformly grown on NNA, rendering the average diameter of NNANCS to be about 2 µm. This size is approximately a magnitude higher than that of nickel nanowire core (diameter about 100 nm, see Figure S3a), suggesting a high mass loading of NiCo₂S₄. Commercial nickel foam (NF) and carbon clothes (CC) were also used as substrates to grow NiCo₂S₄ in a similar method for comparison (see Figure S1 in supporting information). The average diameter of NiCo₂S₄ nanowhiskers on NF and CC is about 50 nm (Figure S1c and Figure S1f), which is larger than that on nickel nanowires. This phenomenon can be attributed to the small size and high aspect ratio of the nickel nanowires, and that the surface of nickel nanowires is curved at nanoscale, while the surfaces of nickel foam and carbon clothes are relatively smooth and planar at nanoscale. The NNANCS electrode shows much superior structural advantages over NF@NiCo₂S₄ (NFNCS) and CC@NiCo₂S₄ (CCNCS), for it has larger specific surface area (the specific surface area of NNANCS, NFNCS and CCNCS are 14.9, 11.8 and 61.30 m² g⁻¹, see Figure S2 in supporting information) for the redox reactions, and it can shorten the transport distance of ions. It is also found that some $NiCo_2S_4$ shed off from the carbon clothes substrate, probably due to the weak interaction between inorganic NiCo₂S₄ and carbon cloth.³²

To investigate the performance of the NNANCS electrode at different mass loadings, the electrode with various mass loadings was prepared by changing the concentration of the solution in the first hydrothermal reaction (see Figure S3 for their SEM images). The composite is able to support an ultrahigh mass loading of 10.57 mg cm^{-2} , which is the highest among $NiCo_2S_4$ based electrodes, to the best of our knowledge.

The morphological characteristic of the composite was revealed by TEM. Figure 3e presents the high-resolution transmission electron microscope (HRTEM) of the NiCo₂S₄ coated on nickel nanowire. The visible lattice fringes with spacings of 0.238 nm and 0.168 nm are attributed to the (311) and (422) planes of the cubic NiCo₂S₄, respectively, which is consistent with the XRD result (Figure 2a). Selected-area electron diffraction (SAED) was conducted to estimate the crystallinity of NiCo₂S₄, which is shown in the inset of Figure 3e. The diffraction rings can be indexed to (311), (400) and (440) planes of the cubic NiCo₂S₄ as marked in Figure 2a, respectively, indicating the polycrystalline structure of NiCo₂S₄. The High Angle Angular Dark Field (HAADF) image of the composite shown in Figure 3f shows the structural characteristic of the composite vividly. Figure 3g-i reveal the corresponding energy dispersive spectrum (EDS) mapping images of Ni, Co and S elements, respectively, showing that the signal of Ni is extremely dense in the middle of the composite, which is attributed to nickel nanowire, while Co and S are evenly distributed throughout the whole composite, suggesting the uniform distribution of NiCo₂S₄ anchored on nickel nanowire. Thus, the SEM and TEM results confirm the successful fabrication of the hierarchical composite, with nickel nanowire as the scaffold to provide fast and efficient electron transport channels, and the needle-like NiCo2S4 to provide rich redox reaction sites. To be noted, the structure of the composite did not break down even after ultrasonic treatment during the process of preparing the TEM samples, which indicates excellent robustness of the composite.

The electrochemical performance of the as-synthesized NNANCS was evaluated in a three-electrode system, with NNANCS directly used as the working electrode, a platinum foil as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and 1 M KOH aqueous solution as the electrolyte. The electrochemical performances of NFNCS and CCNCS electrodes with the same mass loadings to that of the NNANCS electrode (about 4.03 mg cm⁻²) were also tested for comparison. Figure 4a shows the typical cyclic voltammetry (CV) curves of NNANCS at scan rates ranging from 2 mV s⁻¹ to 100 mV s^{-1} with a potential window from -0.1 to 0.5 V (vs. SCE). The well-defined redox peaks indicate redox reactions during the electrochemical process, which implies the pseudocapacitance of the composite material. The peaks show no obvious distortion at a high scan rate up to 100 mV $\rm s^{-1}$ suggesting that the electrode is favourable for fast redox reactions. The peaks in the CV plot of NNANCS may be attributed to the reversible redox reactions of $Co^{2+}/Co^{3+}/Co^{4+}$ and Ni²⁺/Ni³⁺ based on the following reactions:²¹

$$CoS+OH^{-}\leftrightarrow CoSOH+e^{-}$$
(7)

CoSOH+OH⁻↔CoSO+H₂O+e⁻ (8)

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NiS+OH⁻↔NiSOH+e⁻

Figure 4b presents the galvanostatic charge/discharge (GCD) curves of the NNANCS electrode at current densities varying from 1 A g^{-1} to 40 A g^{-1} with a potential window from -0.1 to 0.5 V. The quasi-triangle shapes with voltage plateaus at around 0.2 to 0.3 V indicate the presence of pseudocapacitive behavior and the characteristic of faradaic process of the NNANCS electrode. Based on the GCD results, the corresponding capacitances of NNANCS were measured to be 1523, 1488, 1392, 1285, 1154 and 941 F g^{-1} at current densities of 1, 2, 5, 10, 20, 40 A g^{-1} , respectively, with a rate retention of 61.8% from 1 to 40 A g⁻¹. The CV curves of NNANCS, NFNCS and CCNCS electrodes at the scan rate of 10 mV s⁻¹ are shown in Figure 4c. As can be seen, the CV curve of NNANCS covers the largest area, indicating that it has the highest capacity. The difference of potential (ΔE) between the anodic peak and the cathodic peak in the NNANCS CV curve (about 0.1 V) is smaller than those of NFNCS (about 0.2 V) and CCNCS (about 0.25 V), which indicates that the NNANCS electrode has even better electrochemical reversibility.42 The GCD curves of NNANCS, NFNCS and CCNCS at current density of 5 A g⁻¹ is presented in Figure 4d, from which we can see that the curve of NNANCS presents a symmetric shape with the longest discharge time, which demonstrates better specific capacity and reversibility (detailed data are shown in Figure 4e and 4f). Additionally, the NNANCS electrode shows lower IR drop (about 0.01 V) than those of NFNCS (about 0.04 V) and CCNCS (about 0.2 V), indicating lower resistance. Figure 4e shows the detailed data of the specific mass capacitances of NNANCS, NFNCS and CCNCS as a function of current density. This plot shows that NNANCS has the highest performance among the three, and its capacitance dropped relatively more slowly and almost linearly with the increase of current density, indicating excellent rate capability, while the capacitances of NFNCS and CCNCS dropped more significantly with the increase of current density. Figure 4f demonstrates the cycling stabilities of NNANCS, NFNCS and CCNCS at the current density of 5 A g^{-1} . The NNANCS electrode exhibits a capacitance retention of 92.4% after 20,000 cycles, which is much higher than those of NFNCS (62.7%) and CCNCS (55.6%), and also stands out among nickel cobalt based electrodes (see Table S2). SEM image (Figure S4) shows that its structure is well kept after 20,000 cycles. As has been discussed above, the superior electrochemical performance of the NNANCS electrode can be ascribed to the synergistic effect of ultrathin and highly conductive nickel nanowire and the needle-like NiCo2S4 anchored on it. The highly-conductive NNA can improve the transport and collection of electrons, while the needle-like NiCo2S4 with low intrinsic resistance anchored on nickel nanowire can effectively reduce charge-transfer resistance and provide rich redox sites, and improve electrode-electrolyte contact. Overall, the test-tube-brush-like morphology endows the composite electrode with large surface and fast charge transport capability, which can essentially enhance the performance of pseudocapacitors.⁴³

It is critically important to achieve high specific capacity level at a high electrode mass loading, and the electrochemical properties of NNANCS with different mass loadings are hereby investigated. The CV curves of the composites with various mass loadings at the same scan rate of 10 mV s⁻¹ are presented in Figure 5a, showing that the integrated area in the CV curve increases with the increase of the mass loading of active material. Figure 5b presents the specific mass capacitance and areal capacitance of the composite as a function of mass loading. As predicted, the specific mass capacitance of the composite decreased with the increase of mass loading, but it still retained a relatively high value of 826 F g⁻¹ at an ultrahigh mass loading of 10.57 mg cm^{-2} (the specific mass capacitances of the composites are 1751, 1623, 1523, 1279, and 826 F g^{-1} at mass loadings of 0.81, 2.36, 4.03, 6.82, and 10.57 mg cm^{-2} at the current density of 1 A g⁻¹, respectively). Similarly, the specific areal capacitance of the electrode increased steadily with the increase of mass loading, reaching a value of as high as 8.73 F cm⁻² at the mass loading of 10.57 mg cm⁻² (the areal capacitances of the composites are 1.32, 3.24, 4.83, 6.81, and 8.73 F cm⁻² at mass loadings of 0.81, 2.36, 4.03, 6.82, and 10.57 mg cm⁻² at the current density of 10 mA cm⁻², respectively). This is a relatively high areal capacitance of the ever-reported electrodes, showing great advantage for practical energy storage. Figure 5c presents the Nyquist plots of the composites in open circuit with the frequency ranging from 0.01 to 100,000 Hz with an amplitude voltage of 5 mV. The linear part of the plot in low-frequency region shows the Warburg impedance, which represents the electrolyte and proton diffusion in the active material. The semicircle part of the plot in high-frequency region infers the charge transfer and electrolyte resistances. It can be concluded from Figure 5c that the diameter of the semicircle and the intercept of the curve on the Z'-axis augment with the increase of mass loading. The corresponding $R_{\rm e}$ and $R_{\rm ct}$ of the composite electrodes calculated from the Nyquist plots are presented in Figure 5d, with the inset showing the equivalent circuit. Notably, R_e augmented slowly and linearly with the increase of mass loading, while R_{ct} augmented faster with the increase of mass loading, indicating declined ion diffusion and electron transfer at higher mass loadings. As shown by the SEM images (Figure S3), the NiCo₂S₄ anchored on nickel nanowire became denser and thicker with the increase of mass loading, which can affect both the ion diffusion and electron transfer in the electrode area, thus hindering the full utilization of active materials. This is also consistent with the CV curves of NNANCS with a mass loading of 10.57 mg cm⁻² at scan rates ranging from 2 to 100 mV s⁻¹ (see Figure S5), in which the CV curve distort into fusiform shape at a high scan rate of 100 mV s⁻¹.

To further evaluate the NNANCS composite electrode for practical applications, an asymmetric supercapacitor was fabricated by employing the composite as the positive electrode and activated carbon (AC) as the negative electrode (see experimental section for details). The schematic illustration of the asymmetric supercapacitor is shown in Figure S6, and the CV plot of the activated carbon electrode is shown in Figure S7. The device was tested in a two-electrode

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system. Figure 6a presents the typical CV curves of the device at various scan rates with the potential window from 0 V to 1.6 V. The CV curves exhibit the contributions of both electric double-layer capacitance and pseudocapacitance, and show no obvious distortion at a high scan rate of 100 mV s⁻¹, indicating superior charge/discharge property of the device. Figure 6b shows the GCD curves of the device at current densities ranging from 1 to 40 A $g^{\text{-1}}.$ The quasi-triangular shape with good symmetry suggests that the device has excellent reversibility and capacitive characteristics. Figure 5c shows the Nyquist plot of the device, with the inset showing the details in the high frequency region. The simulated R_e and R_{ct} of the device are about 1.8 Ω and 1.4 Ω , respectively. The nearly vertical part of the plot in low-frequency region indicates excellent ion mobility. The energy and power densities of the device are shown in the Ragone plot in Figure 6d. It can be seen that the device can deliver an energy density as high as 47.29 W h kg⁻¹ at the power density of 793.5 W kg⁻¹, and still a high energy density up to 29.5 W h kg⁻¹ at the maximum power density of 27.64 kW kg⁻¹. The specific energy and power densities are superior to other works related to NiCo₂S₄ (see supporting information table S2). The cycle stability and coulombic efficiency of our device were investigated by repeatedly charging and discharging the device and presented in Figure 6e. The capacity of the device increased a little during the first 1,000 cycles, probably due to the electrolyte wetting process of the AC electrode, and the remarkable capacitance retention of 88.7% after 20,000 cycles stands out among all available $NiCo_2S_4$ based pseudocapacitors, which is almost comparable to electrochemical double-layer capacitors. The excellent electrochemical performance of the device can be attributed to the high capacitance, low intrinsic resistance, and excellent cycling stability of the NNANCS composite electrode. To demonstrate its potential application, the device was employed as the main power to drive light-emitting diodes (LEDs) for evaluation. The photographic images in Figure 6f showed that the device is able to powering 12 LEDs in parallel for 10 minutes both at flat state (Figure 6f(1) to 6f(2)) and at bending state (Figure 6f(3) to 6f(4)). The CV curves of the device stay almost the same under different bending angles (Figure S8). This further confirms that the device not only has preeminent endurance in power, but also has excellent flexibility, which makes it very promising for practical applications.

The outstanding performance of the asymmetric supercapacitor device can be ascribed to the advantages of the test-tube-brush-like NNANCS composite electrode as follows. Firstly, the strong adhesion and synergistic effect of the highly conductive nickel nanowire and the electron conductive NiCo₂S₄ needles provide good pathway for the collection and transfer of electrons. Secondly, the thin NiCo₂S₄ needles can facilitate the intake of electrolyte and shorten the transport distance of ions into the active materials. Thirdly, this electrode shows a unique hierarchical structure; it can not only maximize the utilization of the electrode space and achieve a high mass loading, but also provide periodic channel arrays and rich active sites for redox reactions. Finally, since each of

the "test-tube-brush" are parallel with each other, the structural stability can be highly maintained during charging/discharging and when being bended, which make significant contribution to the superior cycle stability and excellent mechanical flexibility of the electrode.

Conclusions

In summary, we have successfully fabricated the NNANCS composite with a unique test-tube-brush-like hierarchical structure by growing needle-array-like nanowhiskers radially on highly conductive nickel nanowires through a two-step hydrothermal reaction. The composite electrode can not only enhance the electron collection and transfer efficiencies and facilitate the penetration of electrolyte, but also shorten the transport distance of ions and enhance electrode-electrolyte contact, which endows it with a high specific capacitance, excellent rate capability and excellent cycle stability. The electrode performance with different active mass loadings was also investigated, which shows that the electrode can support an ultrahigh mass loading and achieve a high areal capacity. An asymmetric supercapacitor comprising NNANCS and AC also exhibits significant enhancements in energy density and power density; besides, it also possesses additional merits such as lightweight and flexibility, showing great promise for practical applications in various energy storage fields. This work would ultimately promote the design of novel energy storage devices and provide insights into the areas such as flexible electronics. and many other applications.

Conflicts of interest

There are no conflicts to declare.

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Figure 1. Schematic illustration of the synthesis of NNANCS. Firstly, NNA is vertically grown on Ti foil; then, $NiCo2(CO_3)_{1.5}(OH)_3$ is grown on NNA through a hydrothermal reaction in a solution containing Ni/Co salt and urea; finally, $NiCo2(CO_3)_{1.5}(OH)_3$ is in situ transformed into $NiCo_2S_4$ through a second hydrothermal reaction in TAA solution.

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Figure 2. a) XRD pattern of NNA, NNA@precursor and NNANCS. High- resolution XPS spectra of b) Ni 2p, c) Co 2p, and d) S 2p of NNANCS.

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Figure 3. a) to c) SEM images of the composite materials at different magnifications. d) TEM image of NNANCS composite. e) HRTEM image and the SAED pattern (inset) of NiCo₂S₄. f) HAADF of NNANCS and corresponding EDS mapping images of g) Ni, h) Co and i) S elements.

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Figure 4. a) Cyclic voltammetry (CV) curves of NNANCS at scan rates from 2 to 100 mV s¹. b) Galvanostatic charge/discharge (GCD) curves of NNANCS at current densitiesfrom 1 to 40 A g^1 . c) CV curves of NNANCS, NFNCS and CCNCS at scan rate of 10 mV s¹. d) GCD curves of NNANCS, NFNCS and CCNCS at a current density of 5 A g^1 . e)Comparison of the specific capacitance as a function of current density for NNANCS, NFNCS and CCNCS electrodes. f) Comparison of the cycling stability at a current density of10A g^{-1} forNNANCS, NFNCSandCCNCSelectrodes.

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Figure 5. a) CV curves of NNANCS with different mass loadings at a scan rate of 10 mV s⁻¹. b) Galvimetric and areal capacitances of NNANCS as a function of mass loading. c) Nyquist plots of NNANCS with different mass loadings. d) The derived R_e and R_{et} from Nyquist plots as a function of mass loading.

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Figure 6. a) CV curves of the device at scan rates from 2 to 100 mV s⁻¹. b) Galvanostatic charge/discharge (GCD) curves of the device at current densities from 1 to 40 A g^{-1} . c) Nyquist plot of the device; inset shows the plot in high-frequency region. d) The Ragone plot. e) Cycling stability and coulombic efficiency of the device; inset shows the GCD curves of the initial cycles and the last cycles. f) Digital graphs of the device powering 12 LED lights in parallel at flat and bend states.



 $NiCo_2S_4$ nanowhiskers were densely grown on nickel nanowire arrays through hydrothermal process, forming a unique hierarchical test-tube-brush-like composite electrode structure. An asymmetric supercapacitor consisting of this electrode and activated carbon shows the state-of-the-art energy storage performance for $NiCo_2S_4$ -based cathode material at device level.