Controlled synthesis of NiCo₂S₄ nanostructured arrays on carbon fiber paper for high-performance pseudocapacitors

Xunhui Xiong^{1,2}, Gordon Waller¹, Dong Ding¹, Dongchang Chen¹, Ben Rainwater¹,
Bote Zhao¹, Zhixing Wang³, Meilin Liu^{1,2*}

1 School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, Georgia 30332-0245, United States

2 New Energy Research Institute, School of Environment and Energy, South China University of Technology, Guangzhou, Guangdong 510006, China

3 School of Metallurgy and Environment, Central South University, 932 South Lushan Road, Changsha, 410083, P.R. China

* Corresponding Authors: Meilin Liu

E-mail: meilin.liu@mse.gatech.edu

Tel: 404-894-6114; Fax: 404-894-9140;

Abstract: A facile hydrothermal method is utilized to produce nanostructured NiCo₂S₄ arrays on carbon fiber paper with controlled morphologies to study the effect of morphology on their electrochemical performance in supercapacitors. Specifically, NiCo₂S₄ solid nanofiber, nanotube, and hollow nanoneedle of the same crystalline structure are synthesized by controlling the conditions of the hydrothermal synthesis. Among the three different morphologies studied, the hollow nanoneedle of NiCo₂S₄ shows the highest capacity and the longest cycling life, demonstrating a specific capacitance of ~1154 F g⁻¹ at a charge-discharge current density of 1 A g⁻¹ and negligible capacity loss after 8,000 cycles (at a rate of 10 A g⁻¹). This high performance is attributed to the unique nanostructure of the hollow nanoneedle, suggesting that the morphology of NiCo₂S₄ plays a vital role in determining the electrochemical performance. Further, an asymmetric capacitor consisting of NiCo₂S₄ hollow nanoneedle electrode and a tape-cast activated carbon film electrode achieves an energy density of ~17.3 Wh kg⁻¹ at 1 A g⁻¹ and a power density of ~3.2 kW kg⁻¹ at 20 A g⁻¹ in a voltage range of 0 and 1.5 V, implying that it has a great potential for a wide variety of practical applications.

Keywords: capacitor, supercapacitor, NiCo₂S₄, morphology, energy storage, asymmetric capacitor

Introduction

The ever-increasing concerns over environmental pollution and depletion of fossil fuels have stimulated intensive research to develop alternative energy storage and conversion systems with high energy and power density[1-4]. Supercapacitors have attracted great interest in the past decades due to their faster charge and discharge rate and longer cycle life than conventional rechargeable batteries. Since the energy density of carbon-based supercapacitors is about an order of magnitude lower than that of the existing batteries, transition metal oxides, hydroxides, and their compounds have been studied as promising

electrode materials with enhanced charge storage capacity[5-12]. However, these materials usually show compromised rate capability and stability due to low electronic conductivity or structural degradation during cycling. Therefore, it is necessary to develop novel electrode materials to further improve the energy density, rate capability, and operational life.

Recently, transition metal sulfides such as cobalt sulfides and nickel cobalt sulfides have been investigated as promising electrode materials for pseudocapacitors[13-20]. For example, it is shown that NiCo_2S_4 has higher capacity than the corresponding single component sulfides (NiS_x and CoS_x) and displays an electronic conductivity ~ 100 times higher than that of NiCo_2O_4 , although NiCo_2O_4 possesses a much better electronic conductivity than those of NiO and Co_xO_y [21, 22]. Moreover, numerous nanostructures such as nanowires, nanotubes, and nanosheets arrays have been successfully grown on three-dimensional (3D) conductive substrates to increase the utilization of the NiCo_2S_4 electrode material[14-16]. Thus, free-standing and nanostructured NiCo_2S_4 is expected to be a promising electrode material for the next-generation energy-storage devices among all kinds of metal sulfides and metal oxides. To date, however, free-standing NiCo_2S_4 still suffers from significant degradation during cycling[13-15, 20], due most likely to structural and morphological failure. First, the fast and long-term cycling may induce mechanical stress and strain in the NiCo_2S_4 electrode, resulting in delamination of the materials from the substrate. Second, the nanostructured morphology may change due to volume change associated with the ion insertion/desertion process. Thus, morphology can strongly influence the cycle stability of NiCo_2S_4 electrodes. Although NiCo_2S_4 powders with different morphologies, synthesized using different solvents in a hydrothermal proces, showed different capacitances [23], the effect of morphology on the stability of free-standing NiCo_2S_4 electrodes is still to be determined.

In this work, we present a hydrothermal method which enables us to accurately control the morphology of the NiCo_2S_4 nanoarrays on 3D carbon fiber paper by adjusting the precursor solution composition. Specifically, NiCo_2S_4 solid nanofiber, nanotube, and hollow nanoneedle

with identical crystalline structure were created to evaluate the effect of NiCo₂S₄ morphology on the electrochemical performance in supercapacitors. When tested as an electrode in a supercapacitor, all nanostructured NiCo₂S₄ showed reasonably high charge storage capacity, but vastly different cycling stability and capacity retention. Among the three different morphologies studied, the hollow nanoneedle of NiCo₂S₄ showed the highest capacity and the longest cycling life, demonstrating a specific capacitance of ~1154 F g⁻¹ at a charge-discharge current density of 1 A g⁻¹ and negligible capacity loss after 8,000 cycles (at a rate of 10 A g⁻¹). This high performance is attributed to the unique nanostructure of the hollow nanoneedle, suggesting that the morphology of NiCo₂S₄ plays a vital role in determining the electrochemical performance.

Experimental Section

Materials synthesis: All the reagents used in the experiment were of analytical grade and used without further purification. Commercial carbon fiber papers (SpectraCarb 2050 L from Engineered Fibers Technology) were cleaned in 0.1M H₂SO₄ solution prior to deposition. Self-supported nickel cobalt carbonate hydroxide nanowire arrays were prepared by a facile hydrothermal synthesis method described in a previous report[9]. The NiCo₂S₄ arrays were prepared by a second hydrothermal treatment of the as-obtained nickel cobalt carbonate hydroxide nanowire arrays with thioacetamide (TAA). Briefly, 2 mmol TAA was first dissolved in 30 ml deionized water in an 40 ml Teflon container, followed by addition of the nickel cobalt carbonate hydroxide nanowire arrays supported on CFP. Then the autoclave was heated to 140°C for 5 h. After cooling down to room temperature, the NiCo₂S₄ solid nanofiber on CFP was obtained. In order to prepare NiCo₂S₄ nanotube arrays, 2 mmol TAA and 10 mmol urea were dissolved in 30 ml deionized water. After the precursor loaded CFP was inserted in the solution, the autoclave was heated to 90 °C for 5 h to make sure the urea was completely decomposed and then heated to 140 °C for 5 h for the sulfidation process. NiCo₂S₄ hollow nanoneedle arrays were obtained in similar process. 10 mmol urea, 25 mmol

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 50 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2 mmol TAA were added in the 30 ml deionized water, following adding the precursor loaded CFP in Teflon container. The autoclave was heated to 90 °C for 5 h and then 140 °C for 5 h. The mass loading of NiCo_2S_4 nanofibers, nanotubes, and nanoneedles are 1.65, 1.69, and 2.03 mg cm^{-2} , respectively.

Characterization: The phases of the samples were examined by X-ray diffraction (XRD) analysis (PAN'alytical X'Pert Alpha 1, using Cu K- α 1 X-rays). The microstructure and morphology were examined using a scanning electron microscope (LEO 1530 field emission SEM) and a high resolution transmission electron microscope (JEOL 4000 EX). Surface characterization of elemental electronic states was measured by X-ray photoelectron spectroscopy (Thermo K-Alpha XPS, Thermo Fisher Scientific). The instrument was equipped with a monochromatic Al-K α X-ray source ($h\nu = 1468.6$ eV). The spectra were taken in 0.1 eV increments with a beam spot size of 400 μm , constant pass energy of 50 eV, and dwell time of 50ms per increment. Spectra were averaged over at least 4 scans.

Electrochemical Characterization: The electrochemical measurements were carried out in a three electrode electrochemical cell containing 2 M KOH aqueous solution as the electrolyte at room temperature. The NiCo_2S_4 arrays on CFP (1 cm^2) was used as the working electrode. A platinum mesh (1.0 cm^2) and a Ag/AgCl in saturated KCl electrode were used as the counter and the reference electrode, respectively. Cyclic voltammograms were acquired in a potential range between -0.1 and 0.65 V vs REF at different scan rates, and the charge/discharge processes were performed by cycling the potential from 0 to 0.5 V vs REF at different current densities. The cycling stability was evaluated by galvanostatic charge-discharge measurements at a current density of 10 A g^{-1} for over 8000 cycles.

The electrochemical measurements of the asymmetric supercapacitor were carried out to evaluate the NiCo_2S_4 arrays on CFP for practical application in a two-electrode cell in 2 M KOH aqueous electrolyte solution. The CFP supported NiCo_2S_4 is directly used as the positive electrode and the activated carbon film serves as the negative electrode. An activated

carbon film was first prepared by mixing 90 wt% activated carbon and 10 wt% PTFE to form a paste and then rolled into uniform sheet at a thickness of about 20 μm . All the electrochemical measurements were conducted using a Solartron SI 1286 electrochemical workstation.

Results and Discussion

Figure 1 shows the typical fabrication process. The Ni-Co precursor 1D nanowires were vertically grown on the CFP through the reaction between Co^{2+} and Ni^{2+} cations and the hydrolysis products of urea (CO_3^{2-} and OH^-) (Step I in **Figure 1** and **Figure 2a** and **b**). Then the nanowire indexed as metal carbonate hydroxide phase (Supporting Information Figure S1) can be converted to the NiCo_2S_4 nanofiber arrays via acid etching processes (Step II-1 in **Figure 1**), in which H_2S was released from thioacetamide (TAA) in water. As shown in **Figure 2c** and **d**, the array structure is perfectly retained after sulfidation process, but the morphology of the nanowire is replaced by solid nanofiber. When TAA was used as the sulfur source and urea as pH modifier of solution in the hydrothermal process, metal carbonate hydroxide nanowire can be chemically transformed into NiCo_2S_4 nanotubes (Step II-2 in **Figure 1** and **Figure 2e**). The hollow and porous nature can be confirmed by TEM analysis. Another type of morphology was formed when we tried to increase the loading amount of NiCo_2S_4 on CFP by adding TAA, Ni^{2+} and Co^{2+} to form co-precipitated NiCo_2S_4 during the second-step hydrothermal process. Of particular interest, we found that the co-precipitated NiCo_2S_4 will grow on the nanofiber from base to tip and finally form a hollow nanoneedle shape. This was confirmed by the change of morphology achieved by adjusting the added amount of Ni^{2+} and Co^{2+} in the sulfidation process (Figure S2).

Figure 1 Schematic illustration of the fabrication process for NiCo_2S_4 nanostructure arrays with different morphology via two steps.

Before evaluating the effects of morphology on the electrochemical performance, the structure and morphology of the samples were carefully characterized to make sure all NiCo_2S_4 samples of different morphologies had identical crystalline structure. Although the panoramic and magnified FESEM images (**Figure 2**) have showed that the aligned NiCo_2S_4 has different morphologies, TEM analysis was further performed to provide more insight into the detailed microstructures of the as-prepared samples. Typical BFTEM and DFTEM images of NiCo_2S_4 prepared in step II-1 (**Figure 3a** and **b**) show uniform contrast, clearly indicating their solid nature. However, the images of NiCo_2S_4 obtained in step II-2 (**Figure 3e** and **f**) show that these nanorrays have a tube structure at the nanoscale with an internal pore diameter of 60~80 nm. The evolution of hollow structures can be attributed to the Kirkendall diffusion effect, which is widely employed to create interior voids for metal sulfides[24, 25]. Specifically, S^{2-} ions were released from TAA upon emersion in a basic solution due to decomposition of urea. S^{2-} ions react with metal ions to form a thin layer of NiCo_2S_4 on the surface of metal carbonate hydroxide, which then acts as a physical barrier to hinder the direct reaction between outside S^{2-} and inner metal carbonate hydroxide. Accordingly, further reaction is controlled largely by the diffusion of metal ions or S^{2-} through this thin NiCo_2S_4 layer. Since the rate of outward diffusion of the samll metal ions is much greater than the rate

of inward diffusion of the bulky S^{2-} ions, further sulfidation is mostly confined to the outer surface of the $NiCo_2S_4$ layer, creating a hollow structure. Unlike the previous two cases, the $NiCo_2S_4$ obtained in step II-3 are prone to become nanoneedle shape (**Figure 3j** and **k**) because of oriented attachment of co-precipitated $NiCo_2S_4$ (Figure S2) on the existed 1D metal carbonate hydroxide from its base to top. At this low temperature, few S^{2-} ions reacted with existed 1D metal carbonate hydroxide (Figure S3(c)-(d)). At higher temperatures, hollow $NiCo_2S_4$ with an internal pore diameter of ≤ 20 nm formed due to the Kirkendall diffusion of metal ions and S^{2-} through co-precipitated $NiCo_2S_4$ layer. The magnified view of the $NiCo_2S_4$ nanoneedle (Insert in **Figure 3J**) clearly indicates the porous feature. Although the hollow structure is not very easily discernible under BFTEM (**Figure 3k**), DFTEM observation can still identify the continuous hollow and mesoporous structure (**Figure 3k** and Figure S4).

Figure 2 Low- and high-magnification SEM images of (a, b) the precursor-loaded on CFP after the first-step hydrothermal process, (c, d) $NiCo_2S_4$ solid nanofiber, (e, f) $NiCo_2S_4$ nanotube and (h, i) $NiCo_2S_4$ hollow nanoneedle.

Despite the distinct difference in morphology of the three $NiCo_2S_4$ samples (nanofiber, nanotube, and hollow nanoneedle), high-resolution TEM (HRTEM) images of them clearly show the same interplanar distance between the lattice fringes, implying that they have the

identical phase. X-ray powder diffraction (XRD) analysis (Figure S5) of these different materials confirms their phase purity while the molar ratio of metal elements in each compound is determined through energy-dispersive x-ray spectroscopy (EDS) analysis (Figure S6). The results reveal that the as-obtained sample loaded on CFP is NiCo_2S_4 . In the HRTEM image in **Figure 3c, h and l**, lattice fringes are evident from both the center and the edge of a randomly selected NiCo_2S_4 in **Figure 3a, e and j**, respectively. The interplanar distance between the lattice fringes is measured to be 0.542 nm, which can be indexed to (111) crystal planes of NiCo_2S_4 . Additionally, there are notable grain boundaries from the lattice fringes shown in **Figure 3c, h and l**, which indicate that all NiCo_2S_4 arrays are composed of nanocrystals. The SAED patterns of NiCo_2S_4 nanoarrays with the same lattice spacing diffraction rings again indicate the same structure and the polycrystalline nature of the samples.

Figure 3 BFTEM, DFTEM, HRTEM images and SAED patterns of (a-d) NiCo_2S_4 solid nanofiber, (e, i) NiCo_2S_4 nanotube and (j, m) NiCo_2S_4 hollow nanoneedle

To gain further information on the structure and composition, X-ray photoelectron spectroscopy (XPS) was also used to investigate the electronic state of the elements in the near surface region and the corresponding results are presented in **Figure 4**. By using a Gaussian fitting method, the Ni 2p spectra (**Figure 4a**) were best fitted with two spin-orbit

doublets, which are characteristic of Ni^{2+} and Ni^{3+} , and two shakeup satellites (indicated as “Sat.”)[26, 27]. The remarkable difference of the intensity of Ni^{3+} and Ni^{2+} in the $2p_{3/2}$ peak seems to indicate that the majority of Ni element in the crystal lattice is Ni^{3+} . However, the absolute binding energy of the $2p_{3/2}$ peak is not always very helpful in identifying the nickel chemical environment, since relatively small shifts are reported to accompany oxidation of Ni^{2+} to Ni^{3+} . On the contrary, the intense satellite peaks indicate that the majority of Ni element in the crystal lattice is Ni^{2+} cations. As regards the Co 2p spectrum, it shows two distinguished doublets located at a low energy band (Co $2p_{3/2}$) and a high energy band (Co $2p_{1/2}$) and the spin-orbit splitting value of Co $2p_{1/2}$ and Co $2p_{3/2}$ is over 15 eV, suggesting the coexistence of Co^{2+} and Co^{3+} [28, 29]. **Figure 4c** shows the core-level spectrum of the S 2p region, in which the binding energies at 163.1 and 161.8 eV correspond to S $2p_{1/2}$ and S $2p_{3/2}$, respectively. In detail, the peak at 163.5 eV is due to metal-sulfur bonds[30, 31], while the peak at 161.8 eV may be attributed to the S^{2-} in low coordination at the surface. According to the XPS analysis, the near-surface of the three sample has the same composition of Co^{2+} , Co^{3+} , Ni^{2+} , Ni^{3+} , and S^{2-} , which is in good agreement with the formula of NiCo_2S_4 .

Figure 4 XPS spectra of (a) Ni 2p, (b) Co 2p and (c) S 2p for different morphology of NiCo_2S_4 (Upper: solid nanofiber, middle: nanotube, lower: hollow nanoneedle)

The effect of NiCo_2S_4 morphology on the electrochemical performance was investigated via cyclic voltammetry (CV) and galvanostatic charge and discharge testing in a three-

electrode electrochemical cell. As shown in **Figure 5a**, the typical CV curves of all NiCo₂S₄ samples exhibit a pair of well-defined redox peaks within -0.1~0.65 V, suggesting that the capacitance characteristics were mainly governed by Faradaic redox reactions. It is believed that the redox reaction mechanism of NiCo₂S₄ in alkaline electrolyte is via a reversible redox reaction of Ni²⁺/Ni³⁺, Co²⁺/Co³⁺ and Co³⁺/Co⁴⁺ transitions to form NiSOH, CoSOH, and CoSO[32, 33]. The comparison of integrated CV areas indicates that the NiCo₂S₄ hollow nanoneedle possesses a significantly higher specific capacitance than NiCo₂S₄ nanotube or NiCo₂S₄ nanofiber. The rate capability of NiCo₂S₄ is evaluated through CV curves at various potential sweeping rates and galvanostatic charge/discharge at different current densities. At the scan rate of 5 mV s⁻¹, the anodic peak at 0.35 V was ascribed to the oxidation process, and the cathodic peak at about 0.15 V was attributed to its reverse process. The anodic peaks shifted to higher potential while the cathodic peaks shifted to lower potential as the scan rate was increased due to greater ohmic overpotential. From the galvanostatic charge-discharge profiles (**Figure 5c**), it was clear that there were voltage plateaus at around 0.3~0.1 V. The specific galvanostatic capacitances (F·g⁻¹) were calculated from the formula below[6, 34, 35]:

$$C = \frac{2i_m \int V dt}{V^2 |_{V_i}^{V_f}} \quad (1)$$

where $i_m = I/m$ (A·g⁻¹) is the current density, I is the current, m is the active mass of the electrode, V is the potential with an initial and final value of V_i and V_f , respectively. The calculated specific capacitance as a function of the discharge current density was plotted in **Figure 5d**. The specific capacitance is as high as 1154.4 F g⁻¹ when measured at a discharge current density of 1 A g⁻¹ (the current density and specific capacitance were normalized based on the mass of the NiCo₂S₄ hollow nanoneedle and voltage of 0.6 V). The specific capacitance gradually decreased with the increase in current density due to mass transport limitations. However, at higher current densities of 2, 4, 8, 10 and 20 A g⁻¹, the NiCo₂S₄ hollow nanoneedle still showed high specific capacitance of 1105.4, 982.3, 857, 789 and 719

F g^{-1} , which are higher than those for NiCo_2S_4 nanotube (Table S1), NiCo_2S_4 nanofiber, as well as those nanostructured NiCo_2S_4 reported earlier[13, 15-17]. Compared with the nanofiber and nanotube morphologies, the increase in specific capacitance of the NiCo_2S_4 hollow nanoneedle is ascribed to the larger surface area and the unique nanostructure (Figure S7), which endows more active sites for electrochemical reactions and more efficient penetration of electrolyte into the electroactive materials.

Figure 5 Cyclic voltammograms of (a) different morphologies of NiCo_2S_4 at a scan rate of 10 mV s^{-1} and (b) the NiCo_2S_4 hollow nanoneedle electrode at different scan rates from 5 to 30 mV s^{-1} between a voltage window of -0.1 - 0.65 V . (c) constant current discharge curves of NiCo_2S_4 hollow nanoneedle electrode at different current densities. (d) specific capacitances of the different morphologies of NiCo_2S_4 at different current densities

To further determine the effect of NiCo_2S_4 morphology on electrochemical performance, the cycling performance of NiCo_2S_4 nanoarray at current density of 10 A g^{-1} was recorded in the range of 0 - 0.5 V in 2 M KOH aqueous solution (shown in **Figure 6**). The capacitance of NiCo_2S_4 nanofiber fades gradually from 682.5 F g^{-1} for the first cycle to 520.5 F g^{-1} for the 8000^{th} cycle, corresponding to 76.7% capacity retention after $8,000$ cycles. However, the specific capacitance of the NiCo_2S_4 nanotube and NiCo_2S_4 hollow nanoneedle electrodes increased gradually during the first 1300 and 3100 cycles, respectively. The increase in the

specific capacitance may arise from some activation process during the early stage of the charging-discharging cycling[36]. For example, it may take time for the electrolyte to gradually penetrate into the nano-sized pores in the electrodes. As a result, more and more electrode material becomes activated, thus contributing to the increase in specific capacitance. Because of the larger external diameter (especially for the bottom of nanoneedle) and smaller internal pore diameter of the NiCo_2S_4 hollow nanoneedle, the time of activation would be longer and the increase in specific capacitance could be more pronounced. Furthermore, the capacitance increase for the NiCo_2S_4 nanotube and NiCo_2S_4 hollow nanoneedle may also be attributed to the activation process that allows the trapped ions (ions can be trapped between the NiCo_2S_4 crystalline particles during the sulfide process) to gradually diffuse out. After all electrode materials are fully activated, however, the NiCo_2S_4 nanotube electrode exhibited a slight degradation in the subsequent cycles, retaining $\sim 644.7 \text{ F g}^{-1}$ after 8,000 cycles ($\sim 92.8\%$ capacity retention). Similarly, the specific capacitance of the NiCo_2S_4 hollow nanoneedle electrode reached a maximum after activation and then a slight degradation during cycling; however, it maintained $\sim 834.8 \text{ F g}^{-1}$ after 8,000 cycles, suggesting significantly enhanced cycling stability. After multiple tests for each morphology of NiCo_2S_4 , all of the electrodes were carefully washed, dried, and weighed, and the weight loss of the NiCo_2S_4 nanofiber, nanotube, and hollow nanoneedle were 14.5, 5.3, and 1.8wt.%, respectively. For the NiCo_2S_4 nanofiber and nanotube, the capacitance loss is due likely to weak coupling between NiCo_2S_4 and 3D CFP, resulting in delamination of the materials from the substrate (Figure S8a). Additionally, the nanostructured morphology of NiCo_2S_4 remaining on CFP is destroyed due to the volume change during the ion insertion/desertion process. These phenomena are alleviated for NiCo_2S_4 hollow nanoneedle electrode (Figure S8, S9). After long-term cycling, the hierarchical structure of the hybrid nanowire array is preserved, as illustrated in Figure S7c. In this respect, the co-precipitated and oriented growth of NiCo_2S_4 on existed 1D precursor is proposed to serve as a protecting layer to maintain the mechanical strength and

structural integrity during the bulk redox reaction. Interestingly, while the charge storing capability is maintained there is some evolution in the microstructure of the porous surface of NiCo_2S_4 hollow nanoneedle during electrochemical cycling. The surface of these materials becomes rougher, decorated by many tiny nickel cobalt hydroxides “buds” (Figure S10), which is attributed to the formation of nickel cobalt hydroxides on the surface of the nanoneedle while in the alkaline solution[37]. These “buds” are interconnected with each other, forming a more highly porous surface (Figure S8d, S9), which could facilitate fast ion transport, thus enhancing the electrochemical kinetics.

Figure 6 Charge/discharge cycling test at a current density of 10 A g^{-1} for different morphology of NiCo_2S_4 electrodes

To further evaluate the NiCo_2S_4 hollow nanoneedle for practical application, an asymmetric supercapacitor was assembled using the NiCo_2S_4 hollow nanoneedle grown on CFP as the cathode and an tape-cast activated carbon (AC) film as the anode, separated by a glass fiber separator (Figure 7a and b). One advantage of the asymmetric supercapacitor is the use of the pseudocapacitive electrode to enhance the specific capacitance of the cell. On the other hand, the operating voltage of the asymmetric configuration can be extended to around 1.5-2V due to the overpotential of reversible hydrogen electrosorption in a carbon-based negative electrode[38, 39]. In order to improve the practicality of the supercapacitor cell based on NiCo_2S_4 electrode, we applied button cells as the substrate for the supercapacitor. After the

calculation based on the specific capacitance of AC and NiCo₂S₄ hollow nanoneedle obtained in the three-electrode electrochemical cell (Figure S11), 8.69 mg of AC film was chosen to balance the capacitance of a piece of electrode (0.5 cm²).

Figure 7c shows CV curves of an optimized asymmetric supercapacitor at various scan rates of 30, 50, 80, 100, and 150 mV s⁻¹ measured between 0 and 1.5 V in 2 M KOH aqueous electrolyte. The CV curves show well-defined redox peaks between 0~1.5 V, indicating only pseudocapacitive capacitor behavior at all scan rates. Moreover, the cell voltage of the NiCo₂S₄/CFP-AC-based asymmetric supercapacitor was increased to 1.5 V, which is much higher than that of conventional AC-based supercapacitors in aqueous electrolytes (~1 V). This is a critical factor to improve its energy density, considering that the cell energy density is given by $E = 1/2CV^2$, where C represents the specific capacitance and V is the cell voltage. Furthermore, the galvanostatic charge/discharge plots at different current densities with the potential window of 1.5 V are shown in **Figure 7c**. Based on these data, Ragone plot of the device (describing the relationship between energy density and power density) was obtained as shown in **Figure 7d**. The energy and power densities (E and P) were calculated using equations:

$$E = \frac{I \int V dt}{M} \quad (2)$$

$$P = \frac{E}{t} \quad (3)$$

where I is the charge-discharge current, V(t) the cell voltage, dt the time differential, M the mass of the positive electrode (including the mass of CFP), and t the discharging time. The energy density based on the weight of active materials is 86.6 Wh kg⁻¹ at 1 A g⁻¹, which is much higher than that of other asymmetrical supercapacitors reported previously, such as NiCo₂S₄//OMC (ca. 45.5 Wh kg⁻¹)[14], Ni(OH)₂//AC (ca. 50.6 Wh kg⁻¹)[38, 39] and so on. Based on the weight of the positive electrode, a maximum gravimetric energy density and power density of 17.3 Wh kg⁻¹ at 1 A g⁻¹ and 3.2 kW kg⁻¹ at 20 A g⁻¹ are obtained,

respectively, as shown in **Figure 7d**. It is noted however that the loading of active materials is relatively low because the diameters of the carbon fibers are too large. It is highly desirable to grow these hollow NiCo_2S_4 nanoneedles on a suitable scaffold to achieve higher energy density, such as 3D carbon nanofiber paper or 3D graphene with well-connected macroporous structures, large surface area, low mass density, and high electrical conductivity. New results along this direction will be reported in a subsequent communication.

Figure 7 High-performance of hollow nanoneedle NiCo_2S_4 /CFP-AC-based asymmetric supercapacitor. (a) a photograph of the constructed asymmetric supercapacitor; (b) schematic illustration of the ASCs device composed of the NiCo_2S_4 hollow nanoneedle CFP and AC film electrodes; (c) CV curves of ASCs device at various scan rates from 30 to 150 mV s^{-1} measured between 0 and 1.5 V; (d) charge-discharge curves of the asymmetric supercapacitor at various current densities; (e) specific energy and power density of ASCs device evaluated at different charge/discharge rates

Figure 8 demonstrated the super-long life of the asymmetric supercapacitor device up to 12000 times at different current densities, which has rarely been demonstrated for aqueous electrolyte-based asymmetric supercapacitors. In spite of the low initial capacitance, the cell shows continuously increase at an amazing speed at the first 1600th cycles, which we hypothesize to be related to gradually penetration into the porous electrode by electrolyte and the activation process. After 5000 cycles at 10 A g^{-1} , the specific capacitance of the asymmetric supercapacitor was increased from the initial capacitance of 145.6 to 228.1 F g^{-1} ,

demonstrating superior long-term electrochemical stability. After the current density was increased to 20 A g^{-1} , it still possesses a capacitance as high as 141.3 F g^{-1} , and demonstrates an excellent long cycle life without any deterioration after 5000 cycles. When the current returns to 10 A g^{-1} again, 88.6% of the 5000th capacitance (201.2 F g^{-1}) can be recovered and another 2000 cycles without noticeable decrease.

Figure 8 Cycling stability of asymmetric supercapacitor at different current densities. The bottom insets were the charge-discharge profiles for the 2nd, 2500th and 5000th cycle at 10 A g^{-1} and 20 A g^{-1} , respectively

Conclusions

In conclusion, three types of nanostructured NiCo_2S_4 , solid nanofiber, nanotube and hollow nanoneedle have been synthesized and electrochemically evaluated to study the effect of morphology on the electrochemical performance for supercapacitor applications. Among these three morphology, the NiCo_2S_4 hollow nanoneedle provides the highest values of specific capacitance (about 1154.4 F g^{-1} at current density of 1 A g^{-1}), good rate capability, as well as excellent cycling life. The NiCo_2S_4 hollow nanoneedle maintains 107% of the initial value after 8000 cycles, which is ascribed to the mesoporous nature of the hollow nanoneedle morphology and the unique morphology change during cycling. Furthermore, the asymmetric supercapacitor fabricated by NiCo_2S_4 hollow nanoneedle as positive electrode and activated carbon film as negative electrode demonstrated outstanding electrochemical performance, especially when cycled at a high current density. The results suggests the methods we adopted

in our experiments are efficient in studying the effects of the morphology of NiCo₂S₄ nanoarrays on the electrochemical performance for supercapacitor applications, also this method could be extended to the fabrication of other metal sulfide nanostructure arrays. Such an advanced architecture with sulfide hollow nanoneedle grown on substrate can be applicable to more extensive hybrid materials and energy storage and conversion devices.

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