Controlled synthesis of NiCo₂S₄ nanostructures on nickel foams for high-performance supercapacitors

Abstract

A rational synthesis strategy is developed to fabricate hierarchical NiCo₂S₄ nanostructures with controllable mass loadings on Ni foams. The three-dimensional nanoarchitecture ensures good mechanical and electrical connections to increase the ion diffusion and charge transport rate as well as the robust stiffness of the electrode. When used as electrodes for supercapacitors, the novel electrode exhibits outstanding energy storage performance. The specific capacitance is closely associated with the mass loading of the NiCo₂S₄ nanostructures, which manifest 1739 F g⁻¹ at 1 A g⁻¹ along with a maximum areal capacitance of 4.0 F cm⁻², high-rate retention of 85.2% at 30 A g⁻¹ and good cycling stability at an optimal mass loading of 2.3 mg cm⁻². The electrochemical results demonstrate that our NiCo₂S₄ nanostructures are promising electrode materials for high-performance supercapacitor applications.

Keywords: Nanostructure; One-step synthesis; Nickel cobalt sulfide; Supercapacitor; Electrode material

1. Introduction

The ever-growing demands for power sources with high energy/power densities have greatly stimulated extensive research interests on developing high-performance energy storage systems [1, 2]. Supercapacitors, also known as electrochemical capacitors, have received significant attention in widespread potential applications ranging from portable electronics, electrical vehicles to smart utility grids, because of their unique advantages of high power density, fast charge/discharge rate, and a long-span cycle lifetime [3]. Among the device components, electrode materials play a crucial role in determining the supercapacitor performance. The promising candidates generally include porous carbon materials, transition metal oxides, conducting polymers and their derived composites [4-7]. Typically, carbonaceous materials, which store electric energy based on electrochemical double-layer capacitive mechanism, show low specific capacitance [7]. Transition metal oxides and conducting polymers deliver much higher specific capacitance due to their Faradaic redox-induced pseudocapacitive mechanism, but they suffer from either poor electronic conductivity or short cycle life [5, 6, 8]. Therefore, it is imperative to explore a high-performance electrode material with desirable electrochemical properties.

In the search for new electrode materials, transition metal sulfides, such as cobalt sulfides, nickel sulfides and molybdenum sulfides, *etc.*, have been intensively investigated as a new promising class of pseudocapacitive materials for supercapacitors in recent years [9]. The substitution of oxygen with sulfur could create a more flexible structure due to the lower electronegativity of sulfur [10]. In particular, ternary sulfides such as nickel cobalt sulfides (*i.e.*, NiCo_2S_4) are demonstrated to show an electronic conductivity of ~ 2 orders higher than the

ternary metal oxide counterparts (*e.g.*, NiCo_2O_4) [11-13]. More importantly, because of the electrochemical contribution from both nickel and cobalt ions, the ternary sulfides can offer richer redox reaction and higher electronic conductivity compared with the binary metal sulfides of cobalt sulfides and nickel sulfides, resulting in better electrochemical energy storage performance [14, 15]. Recently, a myriad of nickel cobalt sulfides with different nanostructures, such as nanotubes [16-20], nanosheets [14, 21, 22], nanoplates [23, 24], nano-networks [25], urchin-shape nanostructures [11], and hollow structures [26, 27], have been fabricated to show enhanced supercapacitive performance. For example, Lou et al. synthesized NiCo_2S_4 ball-in-ball hollow spheres by a two-step sacrificial template. The hollow spheres exhibited a high specific capacitance of 1036 F g^{-1} at 1.0 A g^{-1} [26]. Zhang et al. reported a similar two-step method to grow NiCo_2S_4 nanosheets on carbon foam. The obtained electrode materials delivered a high specific capacitance of 1231 F g^{-1} at 2 A g^{-1} [21]. Xiao et al. developed a multistep approach to grow NiCo_2S_4 nanotube arrays on carbon fiber paper. The as-formed nanotube array electrode showed a high real capacitance of 0.87 F cm^{-2} at 4 mA cm^{-2} [16]. From the methods that have been established in the literature, the synthesis strategy of NiCo_2S_4 nanostructures is generally based on multistep processes involving hydrothermal preparation of Ni-Co precursors followed by a chemically sulfurization treatment. This strategy not only makes the development of NiCo_2S_4 nanostructures complicated, costly, and time-consuming [12], but also is difficult to control the mass loading of active materials on a three-dimensional (3D) conductive substrate [21], such as Ni foam, carbon foam, and carbon fiber paper.

To address the above-mentioned problems, we herein report a facile scalable synthesis strategy to directly grow NiCo_2S_4 nanostructures onto Ni foams with controllable mass loading.

Owing to the one-step and low-temperature growth characteristics, hierarchical NiCo₂S₄ ultrathin nanosheets with different mass loadings were readily synthesized by changing the reaction dwelling time. The 3D NiCo₂S₄/Ni hybrid nanostructures were investigated as binder-free electrodes for supercapacitors. A high specific capacitance of 1739 F g⁻¹ and a maximum areal capacitance of 4.0 F cm⁻² are achieved at an optimal mass loading of 2.3 mg cm⁻². The as-optimized electrode also manifests good cycling stability and high-rate capacitance retention of 85.2% when the current density increases from 1 to 30 A g⁻¹.

2. Experimental section

2.1 Material synthesis

All chemical reagents were of analytical grade (Sinopharm Chemical Reagent Co. Ltd) and were used without further purification. Ni foam (porosity: 96.5%, pore size: 0.2-0.8 mm, and thickness: 1.6 mm, areal weight: 29±0.3 mg cm⁻²) was purchased from Hefei Kejing Materials Technology. Prior to the synthesis, the Ni foam was first immersed in a 3 M HCl solution for 30 min to get rid of the possible surface oxide layer, and then rinsed with acetone, ethanol and deionized water, respectively. The NiCo₂S₄ nanostructures were prepared via a simple one-step solution-based chemical growth approach. Typically, 1 mmol of Ni(NO₃)₂·6H₂O, 2 mmol of Co(NO₃)₂·6H₂O and 4 mmol of thiourea were dissolved into 40 ml of H₂O/ethylene glycol solvent (1:1 by volume) under magnetic stirring for 30 min, forming a clear pink mixture solution. Subsequently, a piece of as-treated Ni foam was placed into the solution in a sealed vessel, which was transferred to an oven and maintained at a temperature of 90 °C for different hours ranging from 1 to 48 h. After the vessel was naturally cooling down to the room temperature, a dark black foam was received, and washed with deionized water and ethanol for several times. Finally, the samples were dried at

100 °C for 12 h in a vacuum furnace. The mass loading of active materials can be calculated by subtracting the weight of Ni foam before and after reaction, because the Ni foam cannot react with thiourea with other experimental parameters constant. To clarify the role of the Ni foam, a control sample was prepared under the same conditions (reaction time: 12 h) but without the Ni foam. The typical microstructure of the control sample is present in Fig. S1 (Supporting Information).

2.2 Materials characterization

The crystal structure of the sample was examined using X-ray powder diffractometer (XRD, Cu K α radiation, X'Pert PRO MPD, Philips). The morphology was characterized by field-emission scanning electronic microscopy (FE-SEM, Zeiss Supra 55) and transmission electron microscopy (TEM, FEI Tecnai F30G²). The element spectrum was acquired from energy dispersive spectrometer (EDS). The surface chemistry and elemental analysis of the products was obtained on X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific) equipment. All XPS spectra were calibrated with C 1s line at 284.5 eV.

2.3 Electrochemical measurements

The NiCo₂S₄-Ni nanostructures was punched into square discs (10 × 10 mm²), and are used directly as the working electrode. The electrode of the control NiCo₂S₄ powder was fabricated using a conventional slurry-paste method (mass loading: 2.0±0.2 mg cm⁻²). The electrochemical performance of the NiCo₂S₄ was measured at room temperature (~26 °C) in a three-electrode system with 2.0 M KOH, platinum foil and Hg/HgO electrode as the aqueous electrolyte, counter electrode and reference electrode, respectively. Cyclic voltammetry (CV) and galvanostatic charge/discharge tests were performed on a Solartron electrochemical workstation (1260+1287,

England).

3. Results and Discussion

The chemical growth of the NiCo_2S_4 nanostructures is readily controlled by adjusting the reaction dwelling time. Fig. 1(a) and (b) show typical SEM images of the as-prepared sample after a 12 h dwelling time. It is clearly observed that NiCo_2S_4 ultrathin nanosheets with an interconnected nanoscopically porous network are deposited directly onto the macroporous Ni foam. In addition, due to the open framework of 3D Ni foam, NiCo_2S_4 nanosheets can be uniformly and conformally grown throughout the 3D Ni scaffold, as shown in Fig. 1(a), thereby constructing a hierarchical porous architecture. This architecture is beneficial in channeling electrolyte ions to fully access to the porous nanostructures, promoting electrolyte flow in the whole electrode, and reducing ion transport pathways during the charge-discharge operations [12]. The curved nanosheet-like morphology is confirmed by TEM imaging (Fig. 1(c)). The high-resolution TEM image in Fig. 1(d) manifests a piece of nanosheet with a thickness of about 2-3 nm. EDS analysis was carried out to investigate the elemental composition of NiCo_2S_4 nanosheets. Fig. 1(e) exhibits the presence of Ni, Co and S elements, indicating a high purity of the products. The element ratio of Ni/Co/S can be roughly quantified to be approximately 1:1.9:3.7, which matches well with the stoichiometric value of NiCo_2S_4 . The phase structure is further identified by XRD. As shown in Fig. 1(f), except for the two strong peaks of Ni foam, the relatively weak diffraction peaks at 31.4° , 38.4° , 50.1° and 55.2° can be well indexed to the (311), (400), (511), and (440) planes of the cubic phase of NiCo_2S_4 (JCPDS No. 43-1477) [10, 17, 21].

To understand the growth mechanism, NiCo_2S_4 nanostructures were prepared under various reaction dwelling time from 1 to 48 h. Fig. 2(a-e) and **Fig. S2 (Supporting Information)** shows the

corresponding SEM image and XRD patterns of the samples at 1 h, 3 h, 6 h, 24 h, and 48 h, respectively. At the initial stage (1h), the NiCo₂S₄ nanostructures nucleate uniformly onto the Ni surface, and a few pieces of nanosheets start to grow outward sparsely. As the dwelling time increases stepwise to 12 h, more and more nanosheets are growing from the nuclei, forming a highly porous network structure. The nanosheets become thicker when the time extends to 24 h, and finally aggregate to form a dense film consisting of sphere-like nanostructures (48 h). It is noted that the mechanical adhesion of the NiCo₂S₄ nanostructures on Ni foam is robust primarily due to the *in situ* chemically growth approach. Even after dense formation of the NiCo₂S₄ nanostructures (*e.g.*, 48 h), the electrode retains a good porous nature without blocking its macroporous structure. The distinct morphology of NiCo₂S₄ nanostructures is believed to exert great influence on the electrochemical performance when used as a supercapacitor electrode, as will be discussed in the following. More importantly, the one-step synthesis of NiCo₂S₄ nanostructures provides a facile yet effective technique for scale-up production with controllable mass loadings, which holds great advantage compared to the reported multistep preparation methods. The one-step evolution is a typical nucleation and growth process, which is based on the slow hydrolyzation of thiourea that generates hydroxyl ions and sulfur ions [23]. And accordingly, the formation of NiCo₂S₄ nanostructures is resulting from a precipitation of Ni-Co hydroxides and a simultaneous sulfidation process through ion-exchange with sulfur ions. The simple process makes our method time-saving, less costly and loading controllable. Fig. 2(f) shows the mass loading of NiCo₂S₄ nanostructures as a function of dwelling time. It is observed that the mass loading can be modulated from 0.27 ± 0.05 to 5.03 ± 0.25 mg cm⁻² by simply controlling the dwelling time from 1 to 48 h.

Porous architecture of NiCo_2S_4 ultrathin nanosheets is highly desirable for supercapacitor applications. To evaluate the electrochemical capacitive properties, the NiCo_2S_4 nanosheets with different mass loading on nickel foams ($\text{NiCo}_2\text{S}_4@\text{Ni}$) were directly used as conductive additive- and binder-free electrodes. CV and galvanostatic charge/discharge measurements were carried out in a 2 M KOH aqueous electrolyte. Fig. 3(a) shows the CV curves of the $\text{NiCo}_2\text{S}_4@\text{Ni}$ electrodes at the same scan rate of 20 mV s^{-1} . The CV curve shape is typical of pseudocapacitive characteristics associated with Faradaic reactions, as evidenced by the redox couple within the potential range from -0.1 to 0.6 V (vs. Hg/HgO). The positive shift of the oxidation peak for the electrode with a higher mass loading can be attributed to the slow electron/ion transport kinetics (*i.e.*, high polarization resistance) caused by the thicker and denser nanostructures. Notably, the intensity of the areal current increases to a maximum value at the mass loading of 2.3 mg cm^{-2} and then decreases, indicating the electrode with the optimized mass loading of 2.3 mg cm^{-2} can give rise to the best energy storage performance among the studied electrodes. A better understanding of the energy storage mechanism is obtained from the optimized electrode at various scan rates ranging from 2 to 100 mV s^{-1} (Fig. 3(b)). From the CV curve at a low scan rate of 2 mV s^{-1} (inset), two pairs of well-defined redox peaks are observed at around 0.40/0.31 and 0.45/0.40 V for A1/C1 and A2/C2, respectively, which can be attributed to the reversible conversions of $\text{M(II)-S/M(III)-S-OH}$ (M represents Ni or Co) and $\text{Co(III)-S-OH/Co(IV)-S-O}$, respectively [17, 26]. Compared with the electrode with a high mass loading (Fig. S3), the rapid voltammetric response of the optimized electrode can be identified by the visible redox peaks with small potential shifts even at a high scan rate of 100 mV s^{-1} (*e.g.*, 0.31 to 0.25 V for C1 peak), indicating the electrode possesses fast reaction kinetics with low polarization resistance.

The specific capacitance of the active materials is determined using galvanostatic charge/discharge technique. Fig. 3(c) exhibits the resulting charge/discharge voltage profiles of different electrodes at the same current density of 2 A g^{-1} , and Fig. 3(d) shows the optimized electrode (2.3 mg cm^{-2}) at various current densities from 1 to 30 A g^{-1} . The voltage plateaus at 0.35-0.47 V for charge curves and 0.3-0.42 V for discharge curves are consistent with the redox reactions observed in the CV curves. In addition, the discharge curves at different current densities are nearly symmetric to the charge counterparts, revealing a high Coulombic efficiency over 99%. The specific capacitance as a function of the current density is plotted in Fig. 3(e). It is demonstrated that the specific capacitance decreases with the increase in the mass loading. For example, the specific capacitance of the electrode with the lowest mass loading (0.83 mg cm^{-2}) reaches 2732 F g^{-1} (corresponding to a specific capacity of 379 mAh g^{-1}) at 1 A g^{-1} , which is 3.5 times higher than the electrode with the highest mass loading (792 F g^{-1}). In addition, the specific capacitance of the NiCo_2S_4 -Ni electrode with a mass loading of 2.3 mg cm^{-2} is much higher than that of the control electrode of the NiCo_2S_4 powder with a similar mass loading, indicating that the direct growth of NiCo_2S_4 nanostructures on Ni foams is beneficial to improve the electrochemical properties. Generally, a thin layer of active materials could have better electrolyte contact and shorter electron/ion transport distances, resulting in higher electrochemical utilization of active materials and thus higher specific capacitance [3, 28]. However, the high-power performance at the device level depends on the total mass including all of the components in a device [29, 30]. Therefore, it is worthy to reveal the correlation between the areal mass loading of NiCo_2S_4 and the overall performance. Fig. 3(f) shows the areal capacitance of NiCo_2S_4 with different mass loading at various current densities. At a low current density of 1 A g^{-1} , the areal

capacitance increases to a maximum value of about 4.0 F cm^{-2} . As the current density increases, the areal capacitance increases with the NiCo_2S_4 mass until a saturation value is reached at the optimized mass loading of 2.3 mg cm^{-2} . This suggests that the critical areal mass of NiCo_2S_4 is 2.3 mg cm^{-2} in the present study.

Fig. 4(a) summarizes the specific capacitance and areal capacitance of the as-optimized electrode. A high specific capacitance of 1739 F g^{-1} (*i.e.*, 242 mAh g^{-1}) is obtained together with a high areal capacitance of 4.0 F cm^{-2} at 1 A g^{-1} . As the current density increases to 30 A g^{-1} , the electrode still retains about 85.2% of the capacitance (1482 F g^{-1} , or 206 mAh g^{-1}), suggesting a high-rate capability for high-power delivery. The outstanding electrochemical properties combining high specific capacitance and high-rate capability hold great advantage compared to other NiCo_2S_4 -based electrodes in previous reports (see the comparison given in Table S1). The high areal capacitance is also superior to or comparable to other binder-free electrodes, such as 0.87 F cm^{-2} for NiCo_2S_4 nanotubes on carbon fabric [16], 1.13 F cm^{-2} for NiCo_2S_4 nanosheets on carbon fabric [12], 2.84 F cm^{-2} for NiCo_2S_4 nanosheets on carbon foam [21], 3.10 F cm^{-2} for NiCo_2S_4 nanotubes on Ni foam [20], 3.51 F cm^{-2} for NiCo_2O_4 nanosheets on Ni foam [31], 3.12 F cm^{-2} for NiCo_2O_4 nanoneedle array on Ni foam [32], and 3.31 F cm^{-2} for $\text{NiCo}_2\text{O}_4@\text{MnO}_2$ nanoneedle array on Ni foam (more details see Table S2). The superior electrochemical performance can be attributed to the unique architecture of the electrode: (i) the electroactive NiCo_2S_4 nanosheets have intimate electrical connections with the conductive Ni foam supports so that the electrons generated from the Faradaic reactions can be collected and transferred rapidly throughout the electrode; (ii) the ultrathin nanosheets ($\sim 2 \text{ nm}$) greatly reduce the electron/ion transport distances thus enhance the reaction kinetics; and (iii) the hierarchically 3D porous

structure facilitates easy access of electrolyte ions to the porous nanosheets and maximizes electrochemical utilization of the active materials. The cycling performance was further examined by galvanostatic charge/discharge test at 30 A g^{-1} . As shown in Fig. 4(b), the electrode shows a slight increase in the first 200 cycles probably due to the activation process, and then decreases gradually thereafter with 81% retention of its initial capacitance after 3000 cycles.

4. Conclusions

Hierarchical porous NiCo_2S_4 nanostructures have been prepared successfully via a facile and one-step chemical approach. The growth of NiCo_2S_4 nanostructures is controllable and shows significant advantages over the conventional multistep synthesis methods. The NiCo_2S_4 -Ni foams with different mass loadings were investigated as freestanding electrodes for supercapacitors. The optimized electrode with a NiCo_2S_4 mass loading of 2.3 mg cm^{-2} exhibits a high specific capacitance of 1739 F g^{-1} , a maximum areal capacitance of 4.0 F cm^{-2} , high-rate retention of 85.2% at 30 A g^{-1} , and good cycling stability. The outstanding electrochemical performance can be attributed to the highly porous ultrathin nanosheet structure with good mechanical and electrical contact and enhanced ion/electron transport rate. The encouraging results open up a new scalable avenue for fabricating high performance electrode materials for energy storage technologies.

Acknowledgements

The authors acknowledge the financial supports of this work by the National Natural Science Foundation of China (51402236, 53102219), the Natural Science Foundation of Shannxi Province (2015JM5180), the Fundamental Research Funds for the Central Universities

(3102014JCQ01020), and the Program of Introducing Talents of Discipline to Universities (B08040). BQW is grateful for the financial support from the US National Science Foundation (1067960).

References

- [1] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, *Nat. Mater.* 7 (2008) 845-854.
- [2] J. Liu, J.-G. Zhang, Z. Yang, J.P. Lemmon, C. Imhoff, G.L. Graff, L. Li, J. Hu, C. Wang, J. Xiao, G. Xia, V.V. Viswanathan, S. Baskaran, V. Sprenkle, X. Li, Y. Shao, B. Schwenzer, Materials Science and Materials Chemistry for Large Scale Electrochemical Energy Storage: From Transportation to Electrical Grid, *Adv. Funct. Mater.* 23 (2013) 929-946.
- [3] J.-G. Wang, F. Kang, B. Wei, Engineering of MnO₂-based nanocomposites for high performance supercapacitors, *Prog. Mater. Sci.* 74 (2015) 51-124.
- [4] G. Yu, X. Xie, L. Pan, Z. Bao, Y. Cui, Hybrid nanostructured materials for high-performance electrochemical capacitors, *Nano Energy* (2012).
- [5] R. Holze, Y.P. Wu, Intrinsically conducting polymers in electrochemical energy technology: Trends and progress, *Electrochim. Acta* 122 (2014) 93–107.
- [6] D.P. Dubal, R. Holze, Synthesis, properties, and performance of nanostructured metal oxides for supercapacitors, *Pure Appl. Chem.* 86 (2014) 611–632.
- [7] L.L. Zhang, X.S. Zhao, Carbon-based materials as supercapacitor electrodes, *Chem. Soc. Rev.* 38 (2009) 2520–2531.
- [8] W. Wei, X. Cui, W. Chen, D.G. Ivey, Manganese oxide-based materials as electrochemical supercapacitor electrodes, *Chem. Soc. Rev.* 40 (2011) 1697-1721.

- [9] X. Rui, H. Tan, Q. Yan, Nanostructured metal sulfides for energy storage, *Nanoscale* 6 (2014) 9889–9924.
- [10] W. Hu, R. Chen, W. Xie, L. Zou, N. Qin, D. Bao, CoNi₂S₄ Nanosheet Arrays Supported on Nickel Foams with Ultrahigh Capacitance for Aqueous Asymmetric Supercapacitor Applications, *ACS Appl. Mater. Interfaces* 6 (2014) 19318–19326.
- [11] H. Chen, J. Jiang, L. Zhang, H. Wan, T. Qi, D. Xia, Highly conductive NiCo₂S₄ urchin-like nanostructures for high-rate pseudocapacitors, *Nanoscale* 5 (2013) 8879–8883.
- [12] W. Chen, C. Xia, H.N. Alshareef, One-Step Electrodeposited Nickel Cobalt Sulfide Nanosheet Arrays for High-Performance Asymmetric Supercapacitors, *ACS Nano* 8 (2014) 9531–9541.
- [13] Z. Wu, Y. Zhu, X. Ji, NiCo₂O₄-based materials for electrochemical capacitors, *J. Mater. Chem. A* 2 (2014) 14759–14772.
- [14] S. Peng, L. Li, C. Li, H. Tan, R. Cai, H. Yu, S. Mhaisalkar, M. Srinivasan, S. Ramakrishna, Q. Yan, In situ growth of NiCo₂S₄ nanosheets on graphene for high-performance supercapacitors, *Chem. Commun.* 49 (2013) 10178-10180.
- [15] W. Du, Z. Wang, Z. Zhu, S. Hu, X. Zhu, Y. Shi, H. Pang, X. Qian, Facile synthesis and superior electrochemical performances of CoNi₂S₄-graphene nanocomposite suitable for supercapacitor electrodes, *J. Mater. Chem. A* 2 (2014) 9613-9619.
- [16] J. Xiao, L. Wan, S. Yang, F. Xiao, S. Wang, Design Hierarchical Electrodes with Highly Conductive NiCo₂S₄ Nanotube Arrays Grown on Carbon Fiber Paper for High-Performance Pseudocapacitors, *Nano Lett.* 14 (2014) 831-838.
- [17] H. Chen, J. Jiang, L. Zhang, D. Xia, Y. Zhao, D. Guo, T. Qi, H. Wan, In situ growth of

NiCo₂S₄ nanotube arrays on Ni foam for supercapacitors: Maximizing utilization efficiency at high mass loading to achieve ultrahigh areal pseudocapacitance, *J. Power Sources* 254 (2014) 249–257.

[18] D. Cai, D. Wang, C. Wang, B. Liu, L. Wang, Y. Liu, Q. Li, T. Wang, Construction of desirable NiCo₂S₄ nanotube arrays on nickel foam substrate for pseudocapacitors with enhanced performance, *Electrochim. Acta* 151 (2015) 35–41.

[19] H. Wan, J. Jiang, J. Yu, K. Xu, L. Miao, L. Zhang, H. Chen, Y. Ruan, NiCo₂S₄ porous nanotubes synthesis via sacrificial templates- high-performance electrode materials of supercapacitors, *CrystEngComm* 15 (2013) 7649–7651.

[20] J. Pu, T. Wang, H. Wang, Y. Tong, C. Lu, W. Kong, Z. Wang, Direct Growth of NiCo₂S₄ Nanotube Arrays on Nickel Foam as High - Performance Binder - Free Electrodes for Supercapacitors, *ChemPlusChem* 79 (2014) 577-583.

[21] L. Shen, J. Wang, G. Xu, H. Li, H. Dou, X. Zhang, NiCo₂S₄ Nanosheets Grown on Nitrogen-Doped Carbon Foams as an Advanced Electrode for Supercapacitors, *Adv. Energy Mater.* (2014) 1400977.

[22] T. Peng, Z. Qian, J. Wang, D. Song, J. Liu, Q. Liua, P. Wangb, Construction of mass-controllable mesoporous NiCo₂S₄ electrodes for high performance supercapacitors, *J. Mater. Chem. A* 2 (2014) 19376–19382.

[23] J. Yang, W. Guo, D. Li, Q. Qin, J. Zhang, C. Wei, H. Fan, L. Wu, W. Zheng, Hierarchical porous NiCo₂S₄ hexagonal plates: Formation via chemical conversion and application in high performance supercapacitors, *Electrochim. Acta* 144 (2014) 16–21.

[24] J. Pu, F. Cui, S. Chu, T. Wang, E. Sheng, Z. Wang, Preparation and electrochemical

characterization of hollow hexagonal NiCo_2S_4 nanoplates as pseudocapacitors materials, *ACS Sustainable Chem. Eng.* 2 (2014) 809-815.

[25] Y. Liu, J. Zhang, S. Wang, K. Wang, Z. Chen, Q. Xu, Facilely constructing 3D porous NiCo_2S_4 nanonetworks for high-performance supercapacitors, *New J. Chem.* 38 (2014) 4045-4048.

[26] L. Shen, L. Yu, H.B. Wu, X.-Y. Yu, X. Zhang, X.W.D. Lou, Formation of nickel cobalt sulfide ball-in-ball hollow spheres with enhanced electrochemical pseudocapacitive properties, *Nat. Commun.* 6 (2015) 6694.

[27] L. Yu, L. Zhang, H. Wu, X. Lou, Formation of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ Hollow Nanoprisms with Enhanced Pseudocapacitive Properties, *Angew. Chem.* 126 (2014) 3785–3788.

[28] J.-G. Wang, Y. Yang, Z.-H. Huang, F. Kang, Coaxial carbon nanofibers/ MnO_2 nanocomposites as freestanding electrodes for high-performance electrochemical capacitors, *Electrochim. Acta* 56 (2011) 9240-9247.

[29] L. Hu, W. Chen, X. Xie, N. Liu, Y. Yang, H. Wu, Y. Yao, M. Pasta, H.N. Alshareef, Y. Cui, Symmetrical MnO_2 –Carbon Nanotube–Textile Nanostructures for Wearable Pseudocapacitors with High Mass Loading, *Acs Nano* 5 (2011) 8904-8913.

[30] L. Hu, M. Pasta, F.L. Mantia, L. Cui, S. Jeong, H.D. Deshazer, J.W. Choi, S.M. Han, Y. Cui, Stretchable, porous, and conductive energy textiles, *Nano Lett.* 10 (2010) 708-714.

[31] G. Zhang, X.W.D. Lou, General Solution Growth of Mesoporous NiCo_2O_4 Nanosheets on Various Conductive Substrates as High-Performance Electrodes for Supercapacitors, *Adv. Mater.* 25 (2013) 976–979.

[32] G.Q. Zhang, H.B. Wu, H.E. Hoster, M.B. Chan-Park, X.W.D. Lou, Single-crystalline

NiCo₂O₄ nanoneedle arrays grown on conductive substrates as binder-free electrodes for high-performance supercapacitors, *Energy Environ. Sci.* 5 (2012) 9453–9456.

Figure captions

Fig. 1 (a-b) SEM and (c-d) TEM images of NiCo₂S₄ nanosheets (12 h) at different magnifications. (e) EDS spectrum and (f) XRD pattern of NiCo₂S₄ nanosheets.

Fig. 2 SEM images of NiCo₂S₄ nanostructures prepared at different reaction time: (a) 1 h; (b) 3 h; (c) 6 h; (d) 24 h and (e) 48 h. (f) Mass loading of NiCo₂S₄ as a function of reaction dwelling time.

Fig. 3 CV curves of (a) NiCo₂S₄ electrodes with different mass loadings and (b) NiCo₂S₄ electrode with a mass loading of 2.3 mg cm⁻² at various scan rates. Inset is the magnified CV curve at 2 mV s⁻¹. Galvanostatic charge/discharge curves of (c) NiCo₂S₄ electrodes with different mass loadings and (d) NiCo₂S₄ electrode with a mass loading of 2.3 mg cm⁻² at various current densities. (e) Specific capacitance as a function of current density. (f) Areal capacitance as a function of mass loading.

Fig. 4 (a) Specific and areal capacitance of the optimized electrode at different current densities. (b) Cycling performance of the optimized electrode. **Inset is an SEM image of morphology of the disassembled sample after 3000 charge-discharge cycles.**

Fig. 1 (a-b) SEM and (c-d) TEM images of NiCo_2S_4 nanosheets (12 h) at different magnifications. (e) EDS spectrum and (f) XRD pattern of NiCo_2S_4 nanosheets.

Fig. 2 SEM images of NiCo_2S_4 nanostructures prepared at different reaction time: (a) 1 h; (b) 3 h; (c) 6 h; (d) 24 h and (e) 48 h. (f) Mass loading of NiCo_2S_4 as a function of reaction dwelling time.

Fig. 3 CV curves of (a) NCS electrodes with different mass loadings and (b) NiCo₂S₄ electrode with a mass loading of 2.3 mg cm⁻² at various scan rates. Inset is the magnified CV curve at 2 mV s⁻¹. Galvanostatic charge/discharge curves of (c) NiCo₂S₄ electrodes with different mass loadings and (d) NiCo₂S₄ electrode with a mass loading of 2.3 mg cm⁻² at various current densities. (e) Specific capacitance as a function of current density. (f) Areal capacitance as a function of mass loading.

Fig. 4 (a) Specific and areal capacitance of the optimized electrode at different current densities. (b) Cycling performance of the optimized electrode. **Inset is an SEM image of morphology of the disassembled sample after 3000 charge-discharge cycles.**

Controlled synthesis of NiCo₂S₄ nanostructures on nickel foams for high-performance supercapacitors

Jian-Gan Wang ^a, Rui Zhou ^a, Dandan Jin ^a, Keyu Xie ^a, Bingqing Wei ^{a, b *}

^a State Key Laboratory of Solidification Processing, Center for Nano Energy Materials, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China. Corresponding Author. E-mail: weib@udel.edu

^b Department of Mechanical Engineering, University of Delaware, Newark, DE19716, USA