1 **Hierarchically Porous CoFe₂O₄ Nanosheets Supported on Ni Foam**
2 **with Excellent Electrochemical Properties for Asymmetric**
3 **Supercapacitors**

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9
10 **Abstract:** A new type of hierarchically mesoporous cobalt ferrite oxide nanosheets,
11 CoFe₂O₄ nanosheets, has been successfully fabricated via a simple hydrothermal method on the Ni
12 foam followed by a post-annealing treatment. This CoFe₂O₄ nanosheets was employed as a
13 supercapacitor electrode and exhibited an excellent capacitance of 503 F g⁻¹ at a current density of
14 2 A g⁻¹. When the current density increased to 20 A g⁻¹, the capacitance of CoFe₂O₄ nanosheets can
15 maintain 78.5% (395 F g⁻¹) of the initial value, indicating the remarkable rate capability of the
16 as-prepared CoFe₂O₄ nanosheets. An aqueous asymmetric supercapacitor (ASC) based on
17 CoFe₂O₄ nanosheets as a positive electrode and the activated carbon (AC) as a negative electrode
18 was assembled for the first time. The as-fabricated ASC delivered a specific capacitance of 73.12
19 F g⁻¹ at a current density of 1.2 A g⁻¹ in a voltage window of 1.5 V. The CoFe₂O₄//AC ASC could
20 achieve a high energy density of 22.85 W h kg⁻¹ and good long-term cycling stability (98%
21 retention after 5000 cycles). These results demonstrated that CoFe₂O₄ nanosheets could be one of
22 the promising electrode materials for supercapacitor applications.

23
24 **Keywords:** CoFe₂O₄ nanosheets, mesopores, asymmetric supercapacitors, electrochemical energy
25 storage.

1. Introduction

Considering the increasing demand for renewable energy resources and their storage, great efforts have been devoted to the development of energy conversion and storage devices in high power density and long cycling life.[1-3] Supercapacitors, as promising energy storage devices, have been of interest for their long lifespan compared to secondary batteries, high capacitance and excellent reliability compared to conventional dielectric capacitors.[4] The performances of supercapacitors largely rely on their electrode materials in compositions and structures. There are two supercapacitors differing in their energy storage mechanisms. Electrochemical double-layer capacitors (EDLCs) accumulate charges in their electrode/electrolyte interface, and pseudocapacitors handle charges via the fast and reversible redox reactions on electrochemically active sites.[5-8] Conducting polymers such as polyaniline[9] and metal oxides such as Co_3O_4 , [10] NiO [11] can be applied as the electrode materials for pseudocapacitors and offer a much higher specific capacitance. Besides simple monometallic oxides, bimetallic transition oxides have recently drawn growing attention in the electrochemical energy storage. They present many unique properties such as achievable oxidation states, high electrical conductivities because of the coexistence of two different cations in a single crystal structure. Moreover, the performance of energy storage devices also significantly depends on the morphology and structure of their electrode materials. The two-dimensional nanostructures, such as nanosheets, have large surface area to afford more efficient electrochemical active sites to shorten the transport/diffusion path lengths for ions and electrons and to improve the structural stability.

Among bimetallic transition oxides, spinel-type cobaltites ($\text{M}_x\text{Co}_{3-x}\text{O}_4$) (M means metal, $0 \leq x \leq 3.0$) possess a better electrical conductivity and higher electrochemical activity than monometallic oxides. The significant enhancement of the energy storage performances of $\text{M}_x\text{Co}_{3-x}\text{O}_4$ was derived from a relatively low energy barrier of the electron transport between Co and other cations. Some nanostructured spinel cobaltites, such as NiCo_2O_4 , [12] MnCo_2O_4 , [13] CuCo_2O_4 , [14] ZnCo_2O_4 , [15] and CoFe_2O_4 , [16] were reported to be excellent in capacitive behaviors and long-term cycling stabilities. Among of them, spinel CoFe_2O_4 electrodes have been applied not only in supercapacitors, and also Li-ion batteries by virtue of their low cost, excellent electrochemical performances and environment friendly. Zhang et al. showed that an as-synthesized CoFe_2O_4 platelets in a 2 μm thickness exhibited a specific capacity of 580 mA h g^{-1} up to 2000th cycle at a

rate of 5 A g^{-1} . [16] Liu et al. showed that an as-fabricated CoFe_2O_4 nanomesh arrays directly grown on the Ni foam exhibited a specific capacitance of 1426 F g^{-1} at 1 A g^{-1} . [17] And Z. Wang et al. fabricated CoFe_2O_4 hollow microspheres to increase the high specific capacitance upto 1790 F g^{-1} at 2 A g^{-1} . [18] Overall, the up-to-date best performed supercapacitors using spinel cobaltite is the CoFe_2O_4 hollow microspheres. However, there was no study reported on the utilization of mesoporous CoFe_2O_4 nanosheets as electrode material for assembling a supercapacitor, such as an ASC, to learn its practical application in energy storage.

This work presented uniform CoFe_2O_4 nanosheets were directly grown on Ni foam via a hydrothermal strategy then annealing for 2h at 400°C . The novel synthesis environment involved $\text{Fe}(\text{ClO}_4)_2$, $\text{Co}(\text{NO}_3)_2$ as starting materials and urea as combustion fuel in an optimized hydrothermal condition without any surfactant and template. As active materials for supercapacitors, CoFe_2O_4 nanosheets exhibit an enhanced capacitance of 503 F g^{-1} at a current density of 2 A g^{-1} . An aqueous asymmetric supercapacitor full cell was assembled using CoFe_2O_4 nanosheets as its positive electrode and AC as its negative electrode. The as-assembled ASC device can be operated in a voltage window of 1.5 V and achieved a specific capacitance of 73.12 F g^{-1} at 1.2 A g^{-1} and showed good cycling stability (98% retention after 5000 cycles). The maximum energy density and power density of $\text{CoFe}_2\text{O}_4//\text{AC}$ ASC were $22.85 \text{ W h kg}^{-1}$ and 6000 W kg^{-1} . All these results suggested CoFe_2O_4 nanosheets could be one of the promising material for energy storage device.

2. Experiment Section

2.1. Hydrothermal Synthesis of CoFe_2O_4 nanosheets

All chemicals were used as received. The synthesis of porous cobalt ferrite oxide nanosheets were based on a hydrothermal method and followed by a post-calcination treatment. In a typical procedure, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol), $\text{Fe}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (2 mmol) and 14 mmol urea were added with vigorous stirring to a mixed solvent, which were 20 ml deionized water and 20 ml ethylene glycol. The Ni foam (2cm $\times$ 5cm piece) was ultrasonically cleaned using a concentrated HCl for the removal of the nickel oxide layer. The treated Ni foam was finally cleaned with ethanol, acetone and deionized water in an ultrasound bath (30 min of successive sonication in each). The aforementioned solution, together with the Ni foam, were transferred into a 100 mL Teflon-lined autoclave and heated gradually to 90°C and maintained at the same temperature for 10h. After the

autoclave was cooled to the ambient condition, the as-synthesized material on Ni substrate was taken from the reaction media, washed, dried, and calcined at 400 °C for 2 h in air (2 °C min⁻¹ heating rate).

2.2. Characterizations.

For each of samples, X-ray diffraction (XRD; ARL™ X'TRA Powder Diffractometer, Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$) was recorded at room temperature with a scan step of 0.02, a scanning speed of 0.2 s/step. Scanning electron microscopy (SEM; Model JSM-6510LV, JEOL Ltd., Tokyo, Japan) and transmission electron microscopy (TEM; Model JEM-1400Plus, JEOL Ltd., Tokyo, Japan) were used to characterize the morphologies of samples. The chemical compositions were analyzed by the energy dispersive X-ray spectroscopy (EDX). Raman spectra of samples were collected using a DXR Raman microscope (Thermo DXR, a 780 nm excitation laser and a confocal microscope). The X-ray photoelectron spectroscopy (XPS) measurements were performed with a multi-functional photoelectron spectrometer (Axis Ultra DLD, Kratos) using Al K α radiation. Nitrogen adsorption-desorption isotherms of samples were analyzed using a Micromeritics ASAP2020M+C Analyzer at 77.45 K.

2.3. Electrochemical Measurements.

The mass of grown CoFe₂O₄ nanosheets (active material) was calculated by subtracting the mass of Ni foam. The loading mass of CoFe₂O₄ on the prepared supercapacitor electrode was 0.6 mg cm⁻². The electrochemical performances of samples were investigated in a traditional three-electrode system. Ni Foam with CoFe₂O₄ nanosheets was used as working electrodes (1 cm² immersed area), a platinum foil served as the counter electrode and an Ag/AgCl electrode as the reference electrode. The 3M KOH was applied as the aqueous electrolyte. Cyclic voltammetry (CV) were recorded at a potential window of 0-0.5V, and galvanostatic charge-discharge (GCD) tests were performed between 0 and 0.4V. The CV and galvanostatic charge-discharge tests were conducted using an electrochemical workstation (CHI 660E, Chenhua, Shanghai). All EIS measurements were carried out on Zennium electrochemical workstation (Zahner, INC. Germany). The impedance spectra were recorded under an AC perturbation signal of 5 mV over the frequency range of 0.01 Hz to 100,000 Hz. The specific capacitance (C_s) was calculated using equation (1).

$$C_s = I \times t / (\Delta V \times m) \quad (1)$$

Where I (mA) is the constant discharge current, t (s) is the discharge time, ΔV (V) is the voltage drop upon discharging, and m (mg) is the mass of the active materials.

2.4. Asymmetric supercapacitor

To assemble an asymmetric supercapacitor, the CoFe_2O_4 nanosheets electrode was used as the positive electrode and AC as the negative electrode. The negative electrode was prepared by dispersing 80 wt% AC, 10 wt% carbon black and 10 wt% poly (tetrafluoro-ethylene) (PTFE) in ethanol and then pasted the homogeneous paste onto a Ni foam by a spatula, then dried at 80°C for 12h. The two electrodes of the ASC were separated by a separator (NKK, MPF20AC-100), and a 3M KOH was used as the electrolyte. The mass of positive and negative electrodes were adjusted according equation (2).

$$C_+ \times \Delta V_+ \times m_+ = C_- \times \Delta V_- \times m_- \quad (2)$$

Where C in F g^{-1} is the specific capacitance of positive or negative electrode, ΔV in V is the potential window, and m in g is the mass of active material. The electrochemical performance of the asymmetric supercapacitor was based on the capacitance obtained from GCD curves. The energy density and power density of the devices were obtained according to the following equations.

$$E = 0.5 C_s (\Delta V)^2 / 3.6 \quad (3)$$

$$P = 3600E / \Delta t \quad (4)$$

Where E is the energy density in Wh kg^{-1} , P is the power density in W kg^{-1} , ΔV in V is the potential window of device, and Δt (s) is the discharge time.

3. Results and Discussion

Figure 1 schematically illustrates the synthesis process of CoFe_2O_4 nanosheets on Ni foam via a hydrothermal method followed by a post-annealing treatment. It is worth mentioning that the nucleation of Fe and Co ions and pressurized environment can facilitate the growth of uniform CoFe_2O_4 nanosheets on Ni foam. Without the interaction of Fe and Co ions, the individual Fe and Co ions can only grow on Ni foams irregularly as shown in Figure S1. The successful fabrication of CoFe_2O_4 nanosheets was confirmed by XRD and Raman spectrums. As shown in Figure 2a, excluding the peaks marked as “star”, contributed to those of Ni, the remaining peaks at $2\theta = 30.5$, 36.0 , 37.8 , 57.4 , 63.1 and 71.4 can be indexed to the (220), (311), (222), (511), (440) and (620)

reflections of spinel CoFe_2O_4 (JCPDS No:00-022-1068), respectively. The whole diffraction peaks were in good agreement with the previous reports.[19-21] Raman spectroscopy was further performed to investigate the structure and phase composition of the samples. The Raman spectra of CoFe_2O_4 nanosheets (Figure 2b) shows the inverse spinel structure like Fe_3O_4 with cubic $O_h^7(Fd3m)$ symmetry. The characteristic peaks at 186, 313, 478, 567 and 652 cm^{-1} corresponded to T_{1g} -3, E_g , T_{1g} -2, T_{1g} -1 and A_{1g} -1 vibration modes of the CoFe_2O_4 , respectively.[22-24] Both the XRD and Raman spectrums confirmed the successful fabrication of CoFe_2O_4 . In order to characterize the specific surface area and pore structure of CoFe_2O_4 nanosheets, nitrogen absorption-desorption isotherms were performed. As shown in Figure 2c, the existence of hysteresis loops at the relative pressure of 0.5-1.0 P/P_0 suggested the mesoporous property of CoFe_2O_4 nanosheets. The BET specific surface areas of CoFe_2O_4 nanosheets was about 68.3 $\text{m}^2 \text{g}^{-1}$. The inset of Figure 2c shows that the pore-size distribution of CoFe_2O_4 nanosheets was mainly centered at 2-4 nm, also implying the mesoporous structure of the material.

Figure 1. Schematic illustration of the synthesis CoFe_2O_4 nanosheets on Ni foam.

Figure 2. (a) XRD patterns and (b) Raman spectra of CoFe_2O_4 nanosheets on Ni foam; (c) N_2 adsorption-desorption isotherms and inset shows the pore size distribution of CoFe_2O_4 nanosheets.

Figure 3a-c present the morphologies of the as-obtained CoFe_2O_4 nanosheets on the Ni foams. After hydrothermal growth and post-annealing process, uniform CoFe_2O_4 nanosheets with high density grow aggregately on the Ni foam forming a channel opening and interconnecting architecture. Figure S2 a and b show high magnification SEM and EDX analysis of CoFe_2O_4 nanosheets. The thickness of CoFe_2O_4 nanosheets were between 30nm and 60nm. The porous structure and ultrathin property of CoFe_2O_4 nanosheets can shorten the diffusion distance from the external electrolyte to the interior reactive surface, facilitating an efficient, reversible Faradaic redox reaction and improving the utilization rate of electrode material.[25] The atomic ratio of Fe/Co of the CoFe_2O_4 nanosheets was approximately 2:1 according to the EDX data, confirming the formation of CoFe_2O_4 nanosheets. In addition, CoFe_2O_4 nanosheets were also fabricated on a Titanium foil under the same reaction condition. Figure S2 c and d exhibit the CoFe_2O_4 nanosheets on the Titanium foil was 100 nm in an average thickness, 20 μm in width and about 2:1 Fe/Co atomic ratio by EDX data. The transmission electron microscopy (TEM) images further revealed highly porous texture as well as an ultrathin feature of CoFe_2O_4 nanosheets, shown in Figure 3d-f. The magnified images (Figure 3f) clearly shows white spots in 2-4 nm, indicating that the mesopores are uniformly distributed throughout the surface of the nanosheets and consistence to the pore size distribution obtained by the N_2 adsorption-desorption isotherms test. The formation of the pores in the nanosheets were likely attributed to the gas liberation of the decomposition of the precursors during thermal treatment.[26] The images of low magnifications (Figure 3d and 3e) implied that the nanosheets possessed coarse surfaces in which the interconnected nanoparticles formed sheet-like structures.

186 **Figure 3.** (a-c) SEM images of typical CoFe₂O₄ nanosheets on Ni foam and (d-f) TEM images of
 187 CoFe₂O₄ nanosheetsscratched from Ni foam.

XPS was further revealed elemental chemical states and chemical compositions on the surface of CoFe_2O_4 nanosheets. Figure 4a is the full scan elemental survey of CoFe_2O_4 nanosheets, confirming the presence of Co, Fe, O, C and Ni (coming from the Ni foam) elements. Figure 4b manifests the high-resolution O 1s spectra, in which a main peak at 529.8 eV and a low intensity peak at 531.5 eV were observed. The O1 peak at 529.8 eV represented a typical metal-oxygen bond and O2 peak at 531.5 eV corresponded to O in the multiplicity of physis- and chemisorbed water at the surface.[27] Figure 4c shows two core level peaks with a spin-orbit splitting about 15 eV correlated to the Co 2p spectra of CoFe_2O_4 nanosheets. The fitting peaks at 780.1 eV and the satellite peak of 787.5 eV were indexed to Co^{3+} , while the fitting peaks at 781.5 eV and 795.4 eV were associated with Co^{2+} . [28, 29] Figure 4d presents the Fe 2p core level spectra. The Fe $2p_{3/2}$ split into two subpeaks after fitting at 710.6 and 712.7 eV (main peaks, Fe^{3+}) with a “shoulder” satellite peak at 718.3 eV (satellite peaks, Fe^{2+}). The fitting peak of Fe $2p_{1/2}$ at 724.5 eV was indexed to Fe^{3+} . [30] The XPS spectra revealed the surface of the as-prepared CoFe_2O_4 nanosheets was a mixed valence compound, which possessed a composition containing Co^{2+} , Co^{3+} , Fe^{2+} and Fe^{3+} .

Figure 4. XPS spectra of the (a) survey, (b) O 1s (c) Co 2p, and (d) Fe 2p regions of CoFe₂O₄ nanosheets on Ni foam.

The electrochemical performances of the CoFe₂O₄ nanosheets grown on Ni foam were evaluated as binder-free electrodes for supercapacitors. The typical CV curves of the CoFe₂O₄ nanosheets were obtained at different scan rates of 5, 10, 20, 40, 60, 80 and 100 mV s⁻¹, as shown in Figure 5a. The CV curves of CoFe₂O₄ nanosheets were deviated from rectangular character within the potential windows ranging from 0 to 0.5V, indicating the pseudocapacitive behavior of the electrode. The shapes of these CV curves showed no significant change as the scan rate increasing, suggesting the excellent reversibility of the Faradaic redox reaction. The redox current almost increased linearly with the increase of scan rate, indicating the redox reaction was a diffusion-controlled process and the kinetics of interfacial Faradic redox reactions were efficient.[31] Figure S3 shows the CV curves of the CoFe₂O₄ nanosheets electrode in comparison to the bare Ni foam electrode at a scan rate of 20 mV s⁻¹, the capacitance of the Ni foam electrode can be negligible compared to the CoFe₂O₄ nanosheets electrode. The property of the electrode was also studied by galvanostatic charge-discharge tests between 0 and 0.4V (vs. Ag/AgCl) at different current densities. Figure 5b shows the charge-discharge curves of CoFe₂O₄ nanosheets at

different current densities. The specific capacitances of the CoFe₂O₄ nanosheets electrode were 503, 482.5, 450, 420, 395 F g⁻¹ at different current densities of 2, 5, 10, 15 and 20 A g⁻¹, respectively. Figure 5(c) shows CV curves of CoFe₂O₄ and its two monometallic counterparts at a common scan rate of 10 mV s⁻¹. The larger CV area of CoFe₂O₄ than those of Co₃O₄ and Fe₃O₄ indicated a superior CoFe₂O₄ in its capacitance. In addition, Figure 5(d) shows typical charge-discharge curves of CoFe₂O₄, Co₃O₄ and Fe₃O₄ at a current density of 2 A g⁻¹, that was in accordance with the aforementioned CV curves. The non-triangular shape of these charge-discharge curves manifested the Faradaic nature of the charge storage mechanism. The plateaus between 0.2V and 0.3V for Fe₃O₄, 0.3 and 0.35 for Co₃O₄ and between 0.28 and 0.32 for CoFe₂O₄ corresponded to the redox peaks in CV curves as shown in Figure 5(c). All samples presented symmetric charge and discharge curves indicating their good coulombic efficiencies. The enhanced electrochemical properties including specific capacitance and conductivity of CoFe₂O₄ nanosheets should be attributed to the coexistence of two different cations in the bimetallic CoFe₂O₄ and its unique nanosheets structure. The redox reaction of CoFe₂O₄ was mainly ascribed to the redox pairs Co(II)/Co(III) and Fe(II)/Fe(III).

CoFe₂O₄ was proposed as following equations:

In Table S1, we compared the performance of CoFe₂O₄ nanosheets with previously reported materials for supercapacitors. The specific capacitance of as-prepared CoFe₂O₄ nanosheets were not only higher than its monometallic oxides, also better than or comparable to those of other bimetallic transition oxides.

Figure 5. (a) CV curves of CoFe₂O₄ nanosheets at different scan rates. (b) Galvanostatic charge-discharge of the CoFe₂O₄ nanosheets at various current densities. (c-f) Comparing bare CoFe₂O₄ electrode (black), Co₃O₄ electrode (red) and Fe₃O₄ electrode (blue), all grown on Ni foam: (c) CV curves at 10 mV s⁻¹, (d) galvanostatic charge-discharge at 2 A g⁻¹, (e) specific capacitances versus discharge current density, and (f) EIS curves (inset shows the EIS curves at high frequency).

The rate capability test and EIS measurement were also carried out to further understand the superior pseudocapacitive performances of CoFe₂O₄ nanosheets electrode. As shown in Figure 5e, when the current density was increased to 20 A g⁻¹, which was 10-fold of the initial value, the capacitance of CoFe₂O₄ nanosheets still remained 395 F g⁻¹. The capacitance retention was 78.5% for CoFe₂O₄ nanosheets, versus 67.4% for Co₃O₄ and 40% for Fe₃O₄, indicating the excellent rate capability of the CoFe₂O₄ nanosheets. The galvanostatic charge-discharge curves of Co₃O₄ and Fe₃O₄ at different current densities can be referred to Figure S4. Figure 5f shows the EIS spectra of all samples with a semicircle at the high-frequency region and a straight line at the low-frequency region. The high-frequency intercept of the semicircle on the real axis can represent the series resistance (R_s) and its diameter can represent the charge-transfer resistance (R_{ct}) of the Faradaic process. Contrasting, the linear part in the low-frequency area is associated with resistance (Warburg resistance W) of electrolyte and ionic diffusion/transport into the electrode surface.[34, 35] The inset of Figure 5f clearly shows that the R_s for CoFe₂O₄ nanosheets, Co₃O₄ and Fe₃O₄ electrodes are 0.56Ω, 0.81Ω and 0.69Ω. In addition, the impedance spectra of CoFe₂O₄ nanosheets electrode revealed a smaller semicircle compared to those of Co₃O₄ and Fe₃O₄ electrodes, indicating that the CoFe₂O₄ electrode possessed a higher charge-transfer conductivity. The greater slope of the straight line in the low-frequency range indicated the prominent capacitive performances.

To further evaluate the practical application potentials of CoFe₂O₄ nanosheets electrode, an aqueous ASC was first assembled using the CoFe₂O₄ nanosheets electrode as a positive electrode and AC as a negative electrode. Figure 6a shows CV curves of AC electrode (black curve) and CoFe₂O₄ nanosheets electrode (red curve) at a scan rate of 20 mV s⁻¹. The rectangular-like shape between -1.0 and 0 V of AC electrode revealed its electrochemical double layer capacitance performance. In order to determine the optimal voltage window of this ASC, the CV measurements of the full cell were conducted within different cell voltages varying from 0-1.1 V to 0-1.5 V (Figure 6b). When the voltage window extended to 1.5 V, the CV curve of full cell still maintained a quasi-rectangular shape. Hence, the voltage window of 0-1.5 V was chosen to investigate the performances of the assembled CoFe₂O₄//AC ASC. Figure 6c shows the CV curves of CoFe₂O₄//AC ASC. When the scan rate was increased, the shape of the CV curves did not change significantly, indicating the high rate capability and good reversibility of the assembled

cell. Figure 6d presents the galvanostatic charge-discharge curves of the ASC in a voltage window of 0-1.5 V. When the current density was higher than 1.6 A g^{-1} , both charge and discharge curves showed a good symmetry, indicating an excellent capacitive character of $\text{CoFe}_2\text{O}_4/\text{AC}$ ASC. The specific capacitances of the $\text{CoFe}_2\text{O}_4/\text{AC}$ ASC were calculated according to the corresponding galvanostatic charge-discharge tests. It was found that the $\text{CoFe}_2\text{O}_4/\text{AC}$ ASC could deliver the maximum specific capacitance of 73.12 F g^{-1} at 1.2 A g^{-1} and still remained 34.13 F g^{-1} at 8 A g^{-1} . The cycling-life test of the $\text{CoFe}_2\text{O}_4/\text{AC}$ ASC was recorded via a continuous charge-discharge at 4.8 A g^{-1} , as shown in Figure 6f. Impressively, the specific capacitance of the full cell still remain 98% of its initial value even after 5000 cycles (more than 150 000s), indicating long lifespan property of this ASC. Figure S5 shows the typical first and last ten charge-discharge cycles of 5000, revealing curves remained undistorted and almost symmetric. In order to further investigate electrochemical stability for the assembled $\text{CoFe}_2\text{O}_4/\text{AC}$ ASC, EIS measurement of the CoFe_2O_4 electrode after cycling test was performed (Figure S6). EIS data implied that the value of R_s increased from 0.56 to $0.85 \text{ }\Omega$ at the high-frequency region. Remarkably, the diameter of the semicircle was decreased after cycling test, revealing an improved charge-transfer conductivity was achieved after cycling tests.

Figure 7a presents the Ragone plot of $\text{CoFe}_2\text{O}_4/\text{AC}$ ASC as well as several typical ASC reported in the literatures. The maximum energy density of $\text{CoFe}_2\text{O}_4/\text{AC}$ ASC in this study was $22.85 \text{ W h kg}^{-1}$ at a power density of 900 W kg^{-1} , and $10.67 \text{ W h kg}^{-1}$ was still maintained even at a high power density of 6000 W kg^{-1} , which was higher than previously reported ASC such as Co_3O_4 NWs//CA (17.9 W h kg^{-1} at 750 W kg^{-1}), [36] NiCo_2O_4 NSs @ HMRA//AC ($15.42 \text{ W h kg}^{-1}$ at 1000 W kg^{-1}), [37] FeCo_2O_4 NWs//AC (20 W h kg^{-1} at about 2000 W kg^{-1}), [33] NiO NSs// Fe_2O_3 NRs (3.64 W h kg^{-1} at 951 W kg^{-1}), [38] $\text{Co}(\text{OH})_2/\text{AC}$ (20.3 W h kg^{-1} at 90.6 W kg^{-1}), [39] $\text{CuCo}_2\text{O}_4/\text{CuO}/\text{AC}$ (13 W h kg^{-1} at 1509 W kg^{-1}) [40] and GNCC//AC (7.6 W h kg^{-1} at 5600 W kg^{-1}). [41] After two $\text{CoFe}_2\text{O}_4/\text{AC}$ ASCs were further connected in series and charged for 10s to about 3.0 V, the connected devices efficiently powered a red LED (1.8 V, 20 mA) and lasted for about 5 min (Figure 7b-c). In order to further study the benefit of asymmetric supercapacitor and the effect of negative electrode for the whole cell. A symmetric supercapacitor (SSC) was also assembled using CoFe_2O_4 nanosheets electrodes as its both positive and negative electrodes, named as $\text{CoFe}_2\text{O}_4/\text{CoFe}_2\text{O}_4$ SSC. The electrochemical properties of $\text{CoFe}_2\text{O}_4/\text{CoFe}_2\text{O}_4$ SSC

310 were studied by CV and GCD tests (Figure S7 a-b). Based on the GCD tests, the
311 $\text{CoFe}_2\text{O}_4//\text{CoFe}_2\text{O}_4$ SSC also achieved a high specific capacitance of 130 A g^{-1} at a current density
312 of 0.5 A g^{-1} . The calculated maximum energy density (Figure S7 c) of $\text{CoFe}_2\text{O}_4//\text{CoFe}_2\text{O}_4$ SSC ,
313 based on the specific capacitance obtained from GCD tests, was $18.08 \text{ W h kg}^{-1}$ at a power density
314 of 250 W kg^{-1} and decreased to 4.8 W h kg^{-1} at a power density of 2500 W kg^{-1} . Obviously, The
315 energy density and power density of $\text{CoFe}_2\text{O}_4//\text{CoFe}_2\text{O}_4$ SSC were lower than those of the
316 $\text{CoFe}_2\text{O}_4//\text{AC}$ ASC, indicating the ASC is an efficient strategy to improve the performances of
317 supercapacitor cell.

318

Figure 6. (a) Comparative CV curves of the activated carbon electrode and CoFe₂O₄ electrode at 20 mV s⁻¹. (b) CV curves at different cell voltages at a scan rate of 20 mV s⁻¹ and (c) different scan rates for CoFe₂O₄// AC-ASC device. (d) Galvanostatic charge-discharge curves at different current densities. (e) Specific capacitances of the CoFe₂O₄//AC-ASC device at different current densities. (f) Cycling stability of CoFe₂O₄//AC-ASC device at a current density of 4.8 A g⁻¹.

Figure 7. (a) Ragone plot of the CoFe₂O₄ //AC-ASC device. The values reported for others devices are given here for a comparison.(b) A digital image showing the two ASC devices in series can lighten up one red LED indicator. (c) Images of the red LED at different stages; powered by the 10 s charged series supercapacitors.

4. Conclusions

In summary, we first time fabricated interconnected CoFe₂O₄ nanosheets supported on Ni foam through viaa facile hydrothermal and followed post-annealing method. The as-fabricated CoFe₂O₄ nanosheets, as a positive supercapacitor electrodes, exhibited a high capacitance of 503 F g⁻¹ at a current density of 2A g⁻¹.An aqueous CoFe₂O₄//AC ASC was further assembled and achieved high specific capacitance of 73.12 F g⁻¹ at 1.2 A g⁻¹ and long life span of 98% retention of its originals specific capacitance after 5000 cycles. The maximum energy density and power density can be up to 22.85 W h kg⁻¹ and 6000W kg⁻¹, respectively. The advantages of CoFe₂O₄ nanosheets electrode, in terms of its high capacitances, excellent cycling stabilities, low-cost and simple fabrication, indicate that CoFe₂O₄ nanosheets electrode can be one of the excellent candidate electrodes for supercapacitors.

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References

- [1] J.R. Miller, P. Simon, Electrochemical capacitors for energy management, *Science Magazine*, 321 (2008) 651-652.
- [2] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, *Nature materials*, 7 (2008) 845-854.
- [3] R.D.L. Smith, M.S. Prévot, R.D. Fagan, Z. Zhang, P.A. Sedach, M.K.J. Siu, S. Trudel, C.P. Berlinguette, Photochemical route for accessing amorphous metal oxide materials for water oxidation catalysis, *Science*, 340 (2013) 60-63.
- [4] X. Ren, C. Tian, S. Li, Y. Zhao, C.-A. Wang, Facile synthesis of tremella-like MnO_2 and its application as supercapacitor electrodes, *Frontiers of Materials Science*, 9 (2015) 234-240.
- [5] G. Yu, L. Hu, M. Vosgueritchian, H. Wang, X. Xie, J.R. McDonough, X. Cui, Y. Cui, Z. Bao, Solution-processed graphene/ MnO_2 nanostructured textiles for high-performance electrochemical capacitors, *Nano letters*, 11 (2011) 2905-2911.
- [6] L. Huang, D. Chen, Y. Ding, S. Feng, Z.L. Wang, M. Liu, Nickel-cobalt hydroxide nanosheets coated on NiCo_2O_4 nanowires grown on carbon fiber paper for high-performance pseudocapacitors, *Nano letters*, 13 (2013) 3135-3139.
- [7] L.L. Zhang, X.S. Zhao, Carbon-based materials as supercapacitor electrodes, *Chemical Society Reviews*, 38 (2009) 2520-2531.
- [8] M. Inagaki, H. Konno, O. Tanaike, Carbon materials for electrochemical capacitors, *Journal of Power Sources*, 195 (2010) 7880-7903.
- [9] D. Mahanta, G. Madras, S. Radhakrishnan, S. Patil, Adsorption and desorption kinetics of anionic dyes on doped polyaniline, *The Journal of Physical Chemistry B*, 113 (2009) 2293-2299.
- [10] Z. Li, Z. Xu, H. Wang, J. Ding, B. Zahiri, C.M.B. Holt, X. Tan, D. Mitlin, Colossal pseudocapacitance in a high functionality-high surface area carbon anode doubles the energy of an asymmetric supercapacitor, *Energy & Environmental Science*, 7 (2014) 1708-1718.
- [11] S. Vijayakumar, S. Nagamuthu, G. Muralidharan, Supercapacitor studies on NiO nanoflakes synthesized through a microwave route, *ACS applied materials & interfaces*, 5 (2013) 2188-2196.
- [12] D. Kong, W. Ren, C. Cheng, Y. Wang, Z. Huang, H.Y. Yang, Three-dimensional NiCo_2O_4 @polypyrrole coaxial nanowire arrays on carbon textiles for high-performance flexible asymmetric solid-state supercapacitor, *ACS applied materials & interfaces*, 7 (2015) 21334-21346.
- [13] Y. Xu, X. Wang, C. An, Y. Wang, L. Jiao, H. Yuan, Facile synthesis route of porous MnCo_2O_4 and CoMn_2O_4 nanowires and their excellent electrochemical properties in supercapacitors, *Journal of Materials Chemistry A*, 2 (2014) 16480-16488.
- [14] S. Liu, K.S. Hui, K.N. Hui, Flower-like Copper Cobaltite Nanosheets on Graphite Paper as High-Performance Supercapacitor Electrodes and Enzymeless Glucose Sensors, *ACS applied materials & interfaces*, 8 (2016) 3258-3267.
- [15] F. Bao, X. Wang, X. Zhao, Y. Wang, Y. Ji, H. Zhang, X. Liu, Controlled growth of mesoporous ZnCo_2O_4 nanosheet arrays on Ni foam as high-rate electrodes for supercapacitors, *RSC Advances*, 4 (2014) 2393-2397.

385 [16] Z. Zhang, W. Li, R. Zou, W. Kang, Y. San Chui, M.F. Yuen, C.-S. Lee, W. Zhang, Layer-stacked
 386 cobalt ferrite (CoFe_2O_4) mesoporous platelets for high-performance lithium ion battery anodes, *Journal*
 387 *of Materials Chemistry A*, 3 (2015) 6990-6997.
 388 [17] L. Liu, H. Zhang, Y. Mu, Y. Bai, Y. Wang, Binary cobalt ferrite nanomesh arrays as the advanced
 389 binder-free electrode for applications in oxygen evolution reaction and supercapacitors, *Journal of*
 390 *Power Sources*, 327 (2016) 599-609.
 391 [18] Z. Wang, W. Jia, M. Jiang, C. Chen, Y. Li, One-step accurate synthesis of shell controllable
 392 CoFe_2O_4 hollow microspheres as high-performance electrode materials in supercapacitor, *Nano*
 393 *Research*, 9 (2016) 2026-2033.
 394 [19] B. Cai, M. Zhao, Y. Ma, Z. Ye, J. Huang, Bioinspired Formation of 3D Hierarchical CoFe_2O_4
 395 Porous Microspheres for Magnetic-Controlled Drug Release, *ACS Applied Materials & Interfaces*, 7
 396 (2015) 1327-1333.
 397 [20] A. Kargar, S. Yavuz, T.K. Kim, C.-H. Liu, C. Kuru, C.S. Rustomji, S. Jin, P.R. Bandaru,
 398 Solution-processed CoFe_2O_4 nanoparticles on 3D carbon fiber papers for durable oxygen evolution
 399 reaction, *ACS applied materials & interfaces*, 7 (2015) 17851-17856.
 400 [21] T.A.S. Ferreira, J.C. Waerenborgh, M. Mendonça, M.R. Nunes, F.M. Costa, Structural and
 401 morphological characterization of FeCo_2O_4 and CoFe_2O_4 spinels prepared by a coprecipitation method,
 402 *Solid State Sciences*, 5 (2003) 383-392.
 403 [22] S.W. Da Silva, T.F.O. Melo, M.A.G. Soler, E.C.D. Lima, M.F. Da Silva, P.C. Morais, Stability of
 404 citrate-coated magnetite and cobalt-ferrite nanoparticles under laser irradiation: a Raman spectroscopy
 405 investigation, *IEEE transactions on magnetics*, 39 (2003) 2645-2647.
 406 [23] M.A.G. Soler, T.F.O. Melo, S.W. Da Silva, E.C.D. Lima, A.C.M. Pimenta, V.K. Garg, A.C.
 407 Oliveira, P.C. Morais, Structural stability study of cobalt ferrite-based nanoparticle using micro Raman
 408 spectroscopy, *Journal of magnetism and magnetic materials*, 272 (2004) 2357-2358.
 409 [24] M.A.G. Soler, E.C.D. Lima, S.W. da Silva, T.F.O. Melo, A.C.M. Pimenta, J.P. Sinnecker, R.B.
 410 Azevedo, V.K. Garg, A.C. Oliveira, M.A. Novak, Aging investigation of cobalt ferrite nanoparticles in
 411 low pH magnetic fluid, *Langmuir*, 23 (2007) 9611-9617.
 412 [25] D.P. Dubal, P. Gomez-Romero, B.R. Sankapal, R. Holze, Nickel cobaltite as an emerging material
 413 for supercapacitors: An overview, *Nano Energy*, 11 (2015) 377-399.
 414 [26] L. Hu, H. Zhong, X. Zheng, Y. Huang, P. Zhang, Q. Chen, CoMn_2O_4 spinel hierarchical
 415 microspheres assembled with porous nanosheets as stable anodes for lithium-ion batteries, *Scientific*
 416 *reports*, 2 (2012).
 417 [27] J.F. Marco, J.R. Gancedo, M. Gracia, J.L. Gautier, E. Rios, F.J. Berry, Characterization of the
 418 nickel cobaltite, NiCo_2O_4 , prepared by several methods: an XRD, XANES, EXAFS, and XPS study,
 419 *Journal of Solid State Chemistry*, 153 (2000) 74-81.
 420 [28] Y. Sharma, N. Sharma, G.V.S. Rao, B.V.R. Chowdari, Studies on spinel cobaltites, FeCo_2O_4 and
 421 MgCo_2O_4 as anodes for Li-ion batteries, *Solid State Ionics*, 179 (2008) 587-597.
 422 [29] M.A. Langell, M.D. Anderson, G.A. Carson, L. Peng, S. Smith, Valence-band electronic structure
 423 of Co_3O_4 epitaxy on CoO (100), *Physical Review B*, 59 (1999) 4791.
 424 [30] Z. Zhou, Y. Zhang, Z. Wang, W. Wei, W. Tang, J. Shi, R. Xiong, Electronic structure studies of the
 425 spinel CoFe_2O_4 by X-ray photoelectron spectroscopy, *Applied Surface Science*, 254 (2008) 6972-6975.
 426 [31] X.-J. Ma, L.-B. Kong, W.-B. Zhang, M.-C. Liu, Y.-C. Luo, L. Kang, Facile fabrication and perfect
 427 cycle stability of 3D NiO@CoMoO_4 nanocomposite on Ni foam for supercapacitors, *RSC Advances*, 4
 428 (2014) 17884-17890.

- [32] E. Laouini, Y. Berghoute, J. Douch, M.H. Mendonça, M. Hamdani, M.I.S. Pereira, Electrochemical behaviour of $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ with ($x=0, 1, 2$ and 3) oxides thin film electrodes in alkaline medium, *Journal of applied electrochemistry*, 39 (2009) 2469.
- [33] A. Pendashteh, J. Palma, M. Anderson, R. Marcilla, Nanostructured porous wires of iron cobaltite: novel positive electrode for high-performance hybrid energy storage devices, *Journal of Materials Chemistry A*, 3 (2015) 16849-16859.
- [34] J. Li, H. Xie, Y. Li, J. Liu, Z. Li, Electrochemical properties of graphene nanosheets/polyaniline nanofibers composites as electrode for supercapacitors, *Journal of Power Sources*, 196 (2011) 10775-10781.
- [35] S.G. Mohamed, T.-F. Hung, C.-J. Chen, C.K. Chen, S.-F. Hu, R.-S. Liu, Efficient energy storage capabilities promoted by hierarchical MnCo_2O_4 nanowire-based architectures, *RSC Advances*, 4 (2014) 17230-17235.
- [36] W. Liu, X. Li, M. Zhu, X. He, High-performance all-solid state asymmetric supercapacitor based on Co_3O_4 nanowires and carbon aerogel, *Journal of Power Sources*, 282 (2015) 179-186.
- [37] X.-F. Lu, D.-J. Wu, R.-Z. Li, Q. Li, S.-H. Ye, Y.-X. Tong, G.-R. Li, Hierarchical NiCo_2O_4 nanosheets@hollow microrod arrays for high-performance asymmetric supercapacitors, *Journal of Materials Chemistry A*, 2 (2014) 4706-4713.
- [38] S. Zhang, B. Yin, Z. Wang, F. Peter, Super long-life all solid-state asymmetric supercapacitor based on NiO nanosheets and $\alpha\text{-Fe}_2\text{O}_3$ nanorods, *Chemical Engineering Journal*, 306 (2016) 193-203.
- [39] S. Yang, K. Cheng, K. Ye, Y. Li, J. Qu, J. Yin, G. Wang, D. Cao, A novel asymmetric supercapacitor with buds-like $\text{Co}(\text{OH})_2$ used as cathode materials and activated carbon as anode materials, *Journal of Electroanalytical Chemistry*, 741 (2015) 93-99.
- [40] A. Shanmugavani, R.K. Selvan, Improved electrochemical performances of $\text{CuCo}_2\text{O}_4/\text{CuO}$ nanocomposites for asymmetric supercapacitors, *Electrochimica Acta*, 188 (2016) 852-862.
- [41] H. Wang, C.M.B. Holt, Z. Li, X. Tan, B.S. Amirkhiz, Z. Xu, B.C. Olsen, T. Stephenson, D. Mitlin, Graphene-nickel cobaltite nanocomposite asymmetrical supercapacitor with commercial level mass loading, *Nano Research*, 5 (2012) 605-617.