Hierarchical Core-Shell Nanosheet Arrays with MnO₂ Grown on Mesoporous CoFe₂O₄ Support for High-Performance Asymmetric Supercapacitors

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ABSTRACT: We demonstrated the design and fabrication of unique core-shell CoFe₂O₄@MnO₂ nanosheets arrays (NSAs) on nickel foam via a facile and scalable method. The CoFe₂O₄ nanosheets (NSs) grown on the nickel foam acted as a porous skeleton with large surface areas for the growth of MnO₂ NSs, achieving the enhancement of both the electrical and the ionic conductivities. Ultrathin MnO₂ NSs were found vertically grown on the CoFe₂O₄ NSs in a core-shell nanoarchitecture. Its thickness can be controlled by retention times during the hydrothermal process. The obtained CoFe₂O₄@MnO₂ NSAs electrode achieved a highly enhanced areal capacitance of 3.59 F cm⁻² at a current density of 2 mA cm⁻². An aqueous asymmetric supercapacitor (ASC) device was assembled using CoFe₂O₄@MnO₂ NSAs as its positive electrode and the activated carbon (AC) as its negative electrode. The as-assembled ASC device can be operated in a voltage region of 1.6V and exhibited a specific capacitance of 103.86 F g⁻¹ at 5 mA cm⁻². Its energy density and power density were as high as 37 W h kg⁻¹ at 470 W kg⁻¹ and 4800 W kg⁻¹ at 15.3 W h kg⁻¹, respectively. These remarkable electrochemical properties suggested that such CoFe₂O₄@MnO₂ NSAs nanoarchitecture could be one of a potential candidates for the next generation energy storage devices with higher energy density delivery.

Keywords: core-shell nanostructure, CoFe₂O₄ nanosheets, MnO₂ nanosheets, asymmetric supercapacitors, energy storage devices

1. Introduction

Severe environmental issues caused by consumption of fossil fuels lead an urgent need to develop clean, efficient and renewable energy sources to maintain a sustainable economic development.[1-3] This calls for the acceleration development of green energy productions, such as solar energy, wind energy and tidal energy. However, these renewable energy resources are unstable and sporadic, suggesting that energy storage devices must be co-existed to keep them in reserve and use them in demands. Supercapacitor is one of the most promising devices for energy storage and has attracted considerable interest in recent years because of its high power density, fast charging-discharging rate and long lifespan.[4-7] In order to satisfy future energy demands for next-generation energy storage applications, the energy density of supercapacitors must be further enhanced without deteriorating their characteristics of long cycling life and high power density.[8, 9] There are several methods to enhance the energy density of supercapacitors, such as enhancing the device capacitance and/or cell potential windows.[10-12] The device capacitance is mainly associated with the electrode materials as well as their morphologies and

structures. In addition, the cell voltage windows depend on materials used in their positive and negative electrodes and electrolytes. Organic electrolytes were reported to expand the voltage window of supercapacitors up to about 3V, but left drawbacks to restrict the commercial application such as the poor conductivity, the higher cost and toxic property.[13] Alternatively, asymmetric supercapacitor (ASC) based on higher ionic conductivities and environmentally friendly aqueous electrolytes has become one of the most efficient and sustainable strategy to improve the potential windows of supercapacitors by achieving benefits of two electrodes.[14] Considering both the capacitance and electrochemical windows are determined by the applied electrode materials, the key toward supercapacitors in both high energy and high power density is to fabricate novel electrode materials with excellent electrochemical properties.

Carbon-based materials are the most common electrode for supercapacitors which are based on rapidly reversible and phase-constant electrochemical double layer capacitor (EDLC) charge storage mechanism. Their major disadvantage is the small specific capacitance and also derivate low energy density.[15, 16] Thus, EDLC has largely been replaced by a new type of supercapacitor, pseudocapacitors, holding the fast and reversible Faradic redox reactions at electrochemically active sites and providing a higher capacitance than carbon-based EDLCs.[17, 18] Among various materials for pseudocapacitors, MnO_2 has been considered as one of the most promising candidates, given its low cost, high theoretical capacity and wide potential window in aqueous electrolyte (1370 F g^{-1} as the oxidation state of Mn ion changes from 4^+ to 3^+ over a potential window of 0.8V).[19] However, single phase and powdered MnO_2 as electrodes severely suffers from its low electrical conductivity, sluggish ionic transport rate and poor cycling stability, which are caused by its phase change and particle aggregation during cycling process.[20] Superior to monometallic oxides, bimetallic transition oxides possess better electrical conductivity and higher electrochemical activity due to the transport of electrons between multiple transition-metal cations in a relatively low activation energy.[21] Thus, bimetallic transition oxides have been considered as effective alternatives in energy storage applications. Among various bimetallic transition oxides, spinel cobaltites, $\text{M}_x\text{Co}_{3-x}\text{O}_4$ materials ($\text{M} = \text{Ni, Zn, Mn, Cu, Fe, } 0 \leq x \leq 3.0$), have been reported to display excellent capacitive behaviors and long-term cycling stabilities.[22-25] Iron (Fe), which is the fourth most common element in the Earth's crust, as a substituent in spinel cobaltites is of great benefit due to its abundant, harmless character. As classic cobalt iron oxides, CoFe_2O_4 and FeCo_2O_4 have been widely demonstrated in both supercapacitors and lithium ion batteries. Recently nanostructured porous wires of FeCo_2O_4 have been applied as positive electrode for supercapacitor, which delivered a specific capacitance of 474 F g^{-1} at 1 A g^{-1} . [26] Liu et al. fabricated CoFe_2O_4 nanomesh arrays directly grown on the nickel foam and achieved a specific capacitance of 1426 F g^{-1} at 1 A g^{-1} . [27] However, the relatively low loading mass ($0.41\text{-}0.64 \text{ mg cm}^{-2}$ for FeCo_2O_4 nanowires, 0.82 mg cm^{-2} for CoFe_2O_4 nanomesh) cannot meet the practical energy capacity in demand.

Nanostructures and composite engineering of materials are two efficient strategies to overcome the drawbacks of different material systems.[28] Combination of these two strategies lead an emerged novel approach to enhance the electrode capacitive performance. This new strategy designs and fabricates an integrated configurations aligned with different material grown on conductive substrates directly.[29] Among various nanoarchitecture, the core-shell structure has been proved to be an efficient strategy to enhance the electrochemical performances of nanocomposites. First of all, the core-shell structure can overcome the drawbacks of the individual component and achieve synergetic improvement such as better electrical conductivity, shorter ionic transport and stronger

mechanical stability. Second, it can prevent particles from agglomerating and increase active sites between electrolyte and electrode.[30] One-dimensional (such as nanowires, nanofibers) and two-dimensional (such as nanosheets) nanostructures have attracted widespread interests to construct core-shell nanostructures because of the high external surface area and good electronic properties. For example, Qiu et al. synthesized $\text{ZnCo}_2\text{O}_4/\text{MnO}_2$ nanocone forests with a mesoporous and hierarchical core-shell structure and achieved specific capacitances of 2339 and 1526 F g^{-1} at current densities of 1 and 10 A g^{-1} , respectively.[31] Bao et al. reported hierarchical $\text{NiCo}_2\text{O}_4@\text{MnO}_2$ core-shell nanosheets arrays via a two-step hydrothermal method achieved a capacitance of 2.39 F cm^{-2} as well as high cycling stability (7.4% loss after 2000 cycles).[32] Based on previous works, these attractive characteristics of core-shell nanostructure can overcome the drawbacks of individual MnO_2 and cobalt iron oxide. Herein, we report a facile and scalable method to fabricate unique $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ core-shell nanosheet arrays on nickel foam as the positive electrode for supercapacitor for the first time. The hybrid $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs displayed an exceptional areal specific capacitance of 3.59 F cm^{-2} ($\approx 1995 \text{ F g}^{-1}$) at a current density of 2 mA cm^{-2} . Moreover, an aqueous asymmetric supercapacitor based on obtained $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs as the positive electrode and AC as the negative electrode was assembled. The optimized $\text{CoFe}_2\text{O}_4@\text{MnO}_2 // \text{AC}$ ASC device achieved a specific capacitance of 103.86 F g^{-1} at 5 mA cm^{-2} . This device can be cycled reversibly in a stable operational voltage of 1.6 V and exhibited a long-term cycling stability (91.5% retention after 2250 cycles). Such an asymmetric supercapacitor can deliver maximum energy density and power density of 37 Wh kg^{-1} and 4800 W kg^{-1} .

2. Experimental

All the chemicals and solvents in this report were analytical grade and used without further purification.

2.1 Synthesis of materials

Synthesis of CoFe_2O_4 NSs on Ni foam

The formation process of CoFe_2O_4 NSs was based on a hydrothermal method, followed by a post-annealing treatment. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) and $\text{Fe}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (2 mmol) in a total 3 mmol and urea in 14 mmol were added to a mixed solvent of deionized water in 15 ml and ethylene glycol in 15 ml with vigorous stirring to obtain Solution A. Nickel foam (2 cm $\times$ 4 cm piece) was carefully cleaned with 6M HCl solution in an ultrasound bath for 5 min in order to remove the nickel oxide layer on its surface and then ultrasonically cleaned using ethanol, deionized and acetone (30 min of successive sonication in each). The as-obtained Solution A together with the nickel foam were transferred into a 50 ml Teflon-lined autoclave, which was heated gradually to 120 $^\circ\text{C}$ and maintained at the same temperature for 7h. After the autoclave cooled down to room temperature naturally, the nickel foam coated with the precursor was rinsed with deionized water and ethanol. The product calcination was finished at 400 $^\circ\text{C}$ for 2h with a heating rate of 2 $^\circ\text{C min}^{-1}$.

Synthesis of MnO_2 NSs on Ni foam

To fabricate bare MnO_2 NSs on Ni foam, 30 ml of 50 mM KMnO_4 aqueous solution was added to a 50 ml Teflon-lined autoclave containing the cleaned nickel foam. The reaction autoclave was sealed and maintained at 160 $^\circ\text{C}$ for 15h. Then the product was rinsed with deionized water and absolute ethanol and dried at 60 $^\circ\text{C}$ for 6h.

Synthesis of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ core-shell NSAs

To prepare $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ core-shell NSAs, 30 ml of 50 mM KMnO_4 aqueous solution was added to a 50 ml

Teflon-lined autoclave containing the nickel foam supported CoFe₂O₄ NSs. The autoclave was kept at 160 °C for 15h. Then the product was rinsed with deionized water and absolute ethanol and dried at 60 °C for 6h.

2.2 Materials characterization

For each of samples, a X-ray diffraction (XRD; ARL™ X'TRA Powder Diffractometer, Cu Kα radiation, λ = 1.5406 Å) was recorded at room temperature with a scan step of 0.02 and a scanning speed of 0.2 s/step. The morphology and structure were characterized by a scanning electron microscopy (SEM; Model JSM-6510LV, JEOL Ltd., Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer (EDX), and a transmission electron microscopy (TEM; Model JEM-2100F, JOEL Ltd., Tokyo, Japan, 200 kV). The X-ray photoelectron spectroscopy (XPS) measurements were performed with a multi-functional photoelectron spectrometer (Axis Ultra DLD, Kratos) using Al Kα radiation. Nitrogen adsorption-desorption isotherms of samples were analyzed using a Micromeritics ASAP2020M+C Analyzer at 77.45 K.

2.3 Electrochemical measurements

The electrochemical experiments were carried out in a three-electrode system in 3M KOH solution as the electrolyte. A platinum foil served as the counter electrode and an Ag/AgCl electrode as the reference electrode. The CoFe₂O₄@MnO₂ NSAs (1 × 1 cm², CoFe₂O₄ mass = 0.6 mg cm⁻², MnO₂ mass = 1.2 mg cm⁻²), CoFe₂O₄ (1 × 1 cm², CoFe₂O₄ mass = 0.6 mg cm⁻²) and MnO₂ (1 × 1 cm², MnO₂ mass = 1.8 mg cm⁻²) were directly used as the working electrodes without any binder or conductive materials (such as carbon black). Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) were recorded on 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. Corresponding area capacitances (C_a), specific capacitances (C_s) are calculated according to the following equations:

$$C_a = I \Delta t / S \Delta V \quad (1)$$

$$C_s = I \Delta t / m \Delta V \quad (2)$$

Where I (A) is the current during the discharge process. Δt(s) is the discharge time, S (cm²) is the area of electrode, m (g) is the mass of electrode materials and ΔV (V) is the potential window.

2.4 Asymmetric supercapacitor

Asymmetric supercapacitor was assembled by integrating CoFe₂O₄ @ MnO₂ NSAs and AC as the positive electrode and negative electrode, respectively. A piece of filter paper was soaked in 3M KOH solution and placed between the positive and negative electrodes as the separator. The negative electrode was firstly 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 1 × 1 cm² Ni foam by a spatula. The obtained AC electrode was pressed and then dried at 80 °C for 24h. In order to achieve optimum asymmetric supercapacitor cell, the mass of the positive and negative electrodes were adjusted according the charge balance theory:

$$C^+ \times \Delta V^+ \times m^+ = C^- \times \Delta V^- \times m^- \quad (3)$$

Where C (F g⁻¹) is the specific capacitance of positive and negative electrode, ΔV (V) is the potential window, and m (g) is the mass of active material. The total mass of active material was about 8.5 mg cm⁻² and the detail calculation was described in the supporting information. 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:

$$E=0.5C_s (\Delta V)^2/3.6 \quad (4)$$

$$P=3600 E/\Delta t \quad (5)$$

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

3. Results and discussions

Figure 1 shows the synthesis process of $CoFe_2O_4@MnO_2$ NSAs schematically. Typically, the synthesizing strategy can be divided into two main steps. $CoFe_2O_4$ NSs on the Ni foam were synthesized via a facile hydrothermal method using the urea as the fuel and following by a post-annealing process. The Ni foam can provide a benign substrate for the nucleation of Fe and Co ions, and the pressurized environment in the hydrothermal process can facilitate the oriented growth of samples. Subsequently, ultrathin MnO_2 NSs were grown on the surface $CoFe_2O_4$ NSs through the heterogeneous nucleation process and finally formed a unique $CoFe_2O_4@MnO_2$ core-shell NSAs. Remarkably, the uniform $CoFe_2O_4$ NSs provided skeleton in a large surface area to grow MnO_2 nanosheets vertically. Without the well-oriented $CoFe_2O_4$ NSs, MnO_2 can only grow on the Ni foam irregularly as shown in Figure S1.

The crystal structures of the as-fabricated samples were characterized using XRD. The black curve in Figure 2a shows the XRD diffraction peaks of $CoFe_2O_4$ NSs on the Ni foam before the MnO_2 growth. Except for the peaks at 44.5° , 52.1° and 76.5° corresponding to Ni foam, the remaining peaks at $2\theta = 30.5^\circ$, 36.0° , 37.8° and 63.2° can be assigned to the (220), (311), (222) and (440) reflections of spinel $CoFe_2O_4$ with the space group of $Fd3m$ (JCPDS No: 22-1086). The diffraction pattern clearly confirm the phase purity of synthesized $CoFe_2O_4$ and was in good accordance to those in previous reports.[27, 33] After the growth of MnO_2 on $CoFe_2O_4$ NSs (red curve), most $CoFe_2O_4$ diffraction peaks still existed except for the reflection of (222) at 37.8° , which may be attributed to partly overlapping the (111) reflection in MnO_2 and (311) reflection in $CoFe_2O_4$. The new peaks at 12.3° and 25.0° can be indexed to (001) and (002) reflections of birnessite-type δ - MnO_2 (JCPDS No: 86-0666). The XRD results revealed the co-existence of δ - MnO_2 and $CoFe_2O_4$ on the Ni foam. The mesoporous properties of the as-fabricated samples were investigated by the surface area and the pore size distribution analysis. As shown in Figure 2b, the N_2 adsorption-desorption isotherms of the $CoFe_2O_4$ and $CoFe_2O_4@MnO_2$ NSAs demonstrated distinct hysteresis loops in the range of 0.5-1.0 P/P_0 , indicating the mesoporous properties of $CoFe_2O_4$ and $CoFe_2O_4@MnO_2$ NSAs. The Brunauer-Emmett-Teller (BET) surface area values of $CoFe_2O_4$ and $CoFe_2O_4@MnO_2$ NSAs were calculated to be about 68 and $156 m^2 g^{-1}$, respectively. After the deposition of MnO_2 nanosheets on the $CoFe_2O_4$, the surface area of active materials was dramatically enlarged which could provide more active sites for the redox reaction. The incremental pore-size distribution of the samples is shown in Figure 2c. Both the $CoFe_2O_4@MnO_2$ NSAs and $CoFe_2O_4$ nanosheets exhibited a pore-size distribution at 2-4 nm, further supporting the mesoporous properties of the prepared samples.

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189 **Figure 1.** Schematic illustration of the synthesis of MnO_2 nanosheets covered CoFe_2O_4 nanosheets on Ni foam.

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192 **Figure 2.** (a) XRD patterns of CoFe₂O₄ nanosheets on Ni foam before (black curve) and after MnO₂ covering (red
193 curve). (b) N₂ adsorption-desorption isotherms and (c) pore-size distribution of CoFe₂O₄ and CoFe₂O₄@MnO₂
194 core-shell NSAs.

The morphologies of CoFe_2O_4 NSs and $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ core-shell NSAs on Ni foam were investigated by the SEM in Figure 3. Panels a and b show SEM images of CoFe_2O_4 NSs at different magnifications. After hydrothermal growth and post-annealing process, uniform CoFe_2O_4 NSs with an average width about $3\mu\text{m}$ grown on the Ni foam and tended to interconnect with each other forming a three-dimensional porous structure. The thickness of CoFe_2O_4 NSs was found around 25nm in the high magnification SEM image (Figure 3b). The porous and ultrathin CoFe_2O_4 NSs provided a favorable condition for the growth of MnO_2 NSs. The typical images of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ core-shell NSAs are presented in Figure 3c and d. The MnO_2 NSs with high density were scarcely packed in the space between CoFe_2O_4 NSs, indicating MnO_2 NSs tended to grow on the surface of CoFe_2O_4 NSs. A high magnification SEM image of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ core-shell NSAs is shown in Figure 3d. It was clear to see MnO_2 in a mean thickness of about 20nm were vertically grown on the surface of CoFe_2O_4 NSs, favoring for the exposure of more active MnO_2 site for electrochemical reaction. In addition, there were a lot of pores existed between core-shell NSAs which can shorten the diffusion distance from the external electrolyte to interior surface and improved the utilization rate of electrode material. Such ultrathin feature and porous structure are beneficial to an efficient, reversible faradaic redox reaction and short ionic diffusion path during the charge-discharge process.[34] The components of CoFe_2O_4 NSs and $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs were confirmed by the EDX spectroscopy (Figure S2a-b). The atomic ratio of Fe/Co of CoFe_2O_4 NSs and $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs were all approximately 2:1 according to EDX data, confirming the formation of CoFe_2O_4 nanosheets. The existence of Mn element in Figure S2b also manifests the formation of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs. The phase and elements in the final product were investigated by SEM and its corresponding element mapping. Figure 3e demonstrated that uniformly distributed elements of Mn, Fe and Co in the whole investigation region. The EDX data (Figure S2c) of the element mapping revealed that the atomic ratio of Fe/Co was about 2:1, and the co-existence of Mn further confirmed the formation of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$.

Figure 3. (a-b) SEM images of typical CoFe_2O_4 nanosheets on Ni foam. (c-d) SEM images of typical CoFe_2O_4 @ MnO_2 core-shell NSAs on Ni foam. (e) SEM image and the corresponding element (Mn, Fe and Co) mapping of the CoFe_2O_4 @ MnO_2 core-shell NSAs.

The nanostructures of the CoFe_2O_4 NSs and $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs were further investigated by TEM. Figure 4a revealed the CoFe_2O_4 NSs with a quasi-rectangular shape corresponding to the SEM image. Importantly, the TEM image also revealed the porous texture and ultrathin feature of the CoFe_2O_4 NSs. The magnified TEM (Figure 4b) clearly showed the uniform mesopores distribution on CoFe_2O_4 NSs, which could likely be caused by the liberation of gases during the decomposition of the precursors. The HRTEM image (Figure 4c) of CoFe_2O_4 NSs shows that the lattice spacing was 0.26 nm, measured from the lattice fringe, which corresponded to the (311) plane of CoFe_2O_4 . The corresponding SAED pattern (inset of Figure 4b) clearly showed the well-defined rings which could be readily ascribed to the (220), (311), (222) (400) and (440) planes of spinel CoFe_2O_4 , respectively. After the growth of MnO_2 NSs on CoFe_2O_4 NSs, the surface of CoFe_2O_4 NSs were covered by MnO_2 NSs. In the Figure 4d, the $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs nanostructure did not show any noticeable separation of MnO_2 , indicating the adhesion of MnO_2 NSs to CoFe_2O_4 NSs could be really firm. The ultrathin property of MnO_2 NSs exhibited in Figure 4e was consistent with those in the SEM observation. The freestanding MnO_2 NSs partly overlapped with each other to form a wrinkled nanostructure. The HRTEM image (Figure 4f) of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs clearly showed that the lattice fringe spaces of 0.19 nm, corresponding to the (111) planes of the birnessite-type $\delta\text{-MnO}_2$. The SAED pattern (inset of Figure 4e) of the nanosheets manifested the polycrystalline feature of $\delta\text{-MnO}_2$. In order to further confirm the core-shell nanostructure of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs, the STEM-EDX mapping of the as fabricated material was performed. Figure 4g shows the EDX mapping analysis of a single $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSA. The co-existence and similar shapes of Mn, O, Fe and Co signals verified the successful fabrication of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ core-shell NSAs.

Figure 4. TEM images of (a-c) CoFe₂O₄ nanosheets and (c-f) CoFe₂O₄ @ MnO₂ NSAs scratched from Ni foam. (The insets in Figure b and e are the corresponding SAED patterns of CoFe₂O₄ nanosheets and CoFe₂O₄@MnO₂ NSAs, respectively.) (g) STEM-EDX mapping of an individual CoFe₂O₄ @ MnO₂ core-shell NSA.

Composite engineering of materials is an important strategy to form high-performance electrode materials for supercapacitors. However, it is worth to point out the adverse effects may also arise during the process of fabricating novel composites. There should be an optimal structure and constituent among the composition of individual substances.[35] In order to optimize performances of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ core-shell NSAs, the thickness of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs was tailored by adjusting the hydrothermal reaction time. Figure 5 shows the SEM images of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs obtained at different reaction times. At the first 5h (Figure 5b), the average thickness of CoFe_2O_4 NSs changes from 25 nm to 70nm, but that of MnO_2 nanosheets were not obvious. Interestingly, the tiny “buds” began to grow on the surface of CoFe_2O_4 NSs according to the high-magnification SEM image. When the reaction time was prolonged to 10 h, the thickness of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSs increased to about 250 nm which was much thicker than that of the 5h test. This enlighten that the tiny “buds” may guide the growth of ultrathin MnO_2 NSs. The relationship of thickness of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSs with reaction times is shown in Figure S3. With the reaction time was prolonged to 20h, the space between core-shell NSAs seemed to be completely occupied by MnO_2 NSs. Smaller pores resulted from thicker covers may restrict the access of electrolyte during charging-discharging, implying an adverse effect for prolonged retention time. This was confirmed in the electrochemical performances of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs with different reaction times in Figure S4a, showing the CV curves of these electrodes at 10 mV s^{-1} . The largest area under the blue curve indicated that $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs for the retention time at 15h was in the highest capacitance. The GCD tests further claimed that the specific capacitance increased initially and then decreased with the increase of the reaction time as shown in Figure 5f. The GCD curves of 5h, 10h and 20h at different current densities are shown in Figure S4b-d.

Figure 5. SEM images of the $\text{CoFe}_2\text{O}_4 @ \text{MnO}_2$ core-shell NSAs obtained at different reaction times: (a) 0h; (b) 5h; (c) 10h; (d) 15h; and (e) 20h. Insets show the high-magnification SEM images. (f) Areal capacitances of $\text{CoFe}_2\text{O}_4 @ \text{MnO}_2$ core-shell NSAs electrodes obtained at different reaction times and at different current densities.

269 The investigation of elemental chemical state and chemical composition on the surfaces of samples helped the
 270 further understandings of its pseudocapacitors mechanism. Figure 6a shows the XPS spectra of Co 2p of CoFe₂O₄
 271 NSs in the binding energy between 773 and 813 eV. There were two main peaks corresponding to Co 2p_{3/2} and Co
 272 2p_{1/2}. The Co 2p_{3/2} can be divided into two subpeaks after fitting. The fitting peaks at 779.9 eV and the satellite
 273 peak of 786.7 eV were indexed to Co³⁺, while the fitting peaks at 781.6 eV and 795.8 eV with the satellite peak of
 274 802.9 eV were associated with Co²⁺. [36] The spin-orbit splitting was approximately 15 eV, suggesting these peaks
 275 were attributed to Co 2p_{3/2} and Co 2p_{1/2}. Figure 6b elucidated the Fe 2p photoionization region between 703 and
 276 741 eV. The Fe 2p_{3/2} yielded two subpeaks after fitting at 710.2 and 712.1 eV (main peaks, Fe³⁺) with a “shoulder”
 277 satellite peak at 717.4 eV (satellite peaks, Fe²⁺). [37] The fitting peak of Fe 2p_{1/2} at 724.6 eV was indexed to Fe³⁺,
 278 while the satellite peak at 733.4 eV was corresponded to Fe²⁺. [37] The XPS characterization clearly revealed the
 279 as-prepared CoFe₂O₄ NSs belonged to the mixed valence compounds, which contained Co³⁺, Co²⁺, Fe³⁺, and Fe²⁺.
 280 The XPS spectra of Mn 2p and O 1s of the deposited MnO₂ are shown in Figure 6c-d, respectively. As shown in
 281 Figure 6c, the Mn 2p_{3/2} and Mn 2p_{1/2} spin-orbit peaks were located at 642.3 and 654.2 eV, which were in good
 282 agreement with the typical MnO₂, implying its +4 oxidation state. [38] By using the fitting method, the O 1s spectra
 283 was well-fitted to be divided into two fitting peaks, representing two kinds of oxygen states named as O1 and O2.
 284 The O1 peak at a binding energy of 529.8 eV can be assigned to a typical metal-oxygen bond. Besides, the fitting
 285 O2 peak at a binding energy of 531.8 eV was caused by the physic- or chemisorbed water at the surface. [39]

286 **Figure 6.** XPS spectra of the (a) Co 2p and (b) Fe 2p regions of CoFe₂O₄ nanosheets. XPS spectra of the (c) Mn 2p
 287 and (d) O 1s of CoFe₂O₄ @ MnO₂ core-shell NSAs.

The electrochemical performances of as-fabricated samples were first conducted in a three-electrode electrochemical system by testing them as working electrodes for supercapacitors. Figure 7a shows CV curves of CoFe₂O₄@MnO₂ NSAs at various scan rates ranging from 5 to 80 mV s⁻¹. With the increasing of scan rates, all CV curves presented a similar shape which deviated from rectangular-like character, demonstrating the pseudocapacitive behavior of the electrode and the excellent interlayer charge transfer and good reversibility features.[40] Figure 7b shows the typically GCD curves of CoFe₂O₄@MnO₂ NSAs at different current densities. The linear slopes and symmetry triangular shapes of the CV curves indicate reversible charge-discharge behavior. The specific area capacitances of the CoFe₂O₄@MnO₂ NSAs electrode were calculated to be 3.59, 3.11, 2.73, 2.14, 1.20, 0.81 F cm⁻² at current densities of 2, 5, 10, 20, 50, 80 mA cm⁻², respectively, according to equation (1). In order to investigate the enhanced performance of unique CoFe₂O₄@MnO₂ core-shell NSAs, we compared the electrochemical properties of CoFe₂O₄ NSs, MnO₂ NSs and CoFe₂O₄@MnO₂ core-shell NSAs. Figure 7 c and d present the CV curves at 20 mV s⁻¹ and GCD curve at 5 mA cm⁻² of aforementioned three samples, respectively. The CV shapes of the individual components NSs indicated the pseudocapacitive property of CoFe₂O₄ NSs and MnO₂ which based on the Faradic redox reaction in their energy storage processes. The redox pairs of Co (III)/Co (II), Co (IV)/Co (III) and Fe (VI)/Fe (III) mainly contribute to the redox reaction of CoFe₂O₄ [41, 42] and the energy storage mechanism can be proposed as following:

Also, it has been well accepted that the energy storage property of MnO₂ could be attributed to its redox reaction based on the redox pairs of Mn (IV)/Mn (III) equation [43, 44]:

Where M⁺ is an alkali cation such as K⁺, Na⁺ and Li⁺. However, The CV shape of CoFe₂O₄@MnO₂ NSAs was different from those of CoFe₂O₄ and MnO₂ and its area was much larger than those of both individual substances, indicating the electrochemical properties of CoFe₂O₄ and MnO₂ can be changed by the formation of CoFe₂O₄@MnO₂ NSAs. The absence of obvious redox peak in CoFe₂O₄@MnO₂ NSAs can be attributed to the change of morphologies and sizes after the deposition of MnO₂ NSs on the CoFe₂O₄ NSs.[45] A comparison of the GCD curves at 5 mA cm⁻² is illustrated in Figure 7d. Obviously, the charge-discharge time of CoFe₂O₄@MnO₂ NSAs was much longer than those of CoFe₂O₄ and MnO₂ NSs electrodes which indicated a much improved capacitance. It can also be seen that the charge-discharge curves of all samples were almost symmetric, suggesting their excellent columbic efficiencies. In order to evaluate the rate capability of CoFe₂O₄@MnO₂ NSAs electrode, we compared the specific area capacitance of all samples at different current densities. When the current density increased to 20 mA cm⁻², which was 10-fold of the initial one, the capacitance CoFe₂O₄@MnO₂ NSAs still remained 2.14 F cm⁻² (Figure 7e). The capacitance retention was about 60% of the original value which was higher than 50% for CoFe₂O₄ NSs and 43.8% for MnO₂ NSs at 20 mA cm⁻², showing the remarkable rate capability of the CoFe₂O₄@MnO₂ NSAs electrode. The GCD curves of CoFe₂O₄ and MnO₂ NSs at different current densities are shown in the Figure S5. In addition, we can see all the specific area capacitances of CoFe₂O₄@MnO₂ NSAs at

different current densities were much higher than the sum of CoFe_2O_4 and MnO_2 NSs which further manifest the formation of core-shell nanostructure was an efficient strategy to enhance the performance of electrode materials. In Table S1 (Supporting Information), we compared the performance of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs electrode with previously reported materials used as positive electrodes in supercapacitors. The specific capacitance of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs was found not only higher than individual CoFe_2O_4 and MnO_2 NSs, also better than most of reported CoFe_2O_4 -based materials $\text{MnO}_2/\text{M}_x\text{Co}_{3-x}\text{O}_4$ materials ($\text{M} = \text{Co}, \text{Ni}, \text{Zn}, \text{Mn}, \text{Cu}, 0 \leq x \leq 3.0$). Electrochemical impedance spectroscopy (EIS) was carried out to study the ion-transport behavior of CoFe_2O_4 NSs, MnO_2 NSs and $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs electrodes. As shown in Figure 7f, all samples presented similar shapes in a semicircle at a higher frequency region and a straight line at lower frequency. At the high frequency, the intersection of the curve on the real axis represents the series resistance (R_s , representing the inherent active material resistance, electrolyte resistance and contact resistance) and the semicircle diameter represents the Faradaic charge transfer resistance (R_{ct}).^[46] R_s values of $0.63 \, \Omega$, $0.53 \, \Omega$ and $0.78 \, \Omega$ can be calculated from EIS curves of the $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs, CoFe_2O_4 NSs and MnO_2 NSs electrodes, respectively. The increased R_s should be attributed to the poor conductivity of MnO_2 . Impressively, the $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs exhibited a smaller semicircle in EIS than MnO_2 NSs electrodes, indicating the faster ion insertion/extraction during electrochemical reactions. The near linear EIS plots of these samples at the low frequency are the characteristic of Warburg impedance (W , reflecting the resistance behavior caused by the diffusion of OH^- within electrode materials during redox reaction).^[47] The more perpendicular line leaning to the real axis of $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs electrode, suggesting more facile electrolyte diffusion to the surface and the ideal capacitive behavior.

Figure 7. (a) CV curves of CoFe₂O₄ @ MnO₂ core-shell NSAs at different scan rates. (b) Galvanostatic charge-discharge of the CoFe₂O₄ @ MnO₂ core-shell NSAs at various current densities. (c-f) Comparing bare CoFe₂O₄ electrode (black), bare MnO₂ electrode (red) and optimal CoFe₂O₄ @ MnO₂ electrode (blue), all grown on Ni foam: (c) CV curves at 20 mV s⁻¹, (d) galvanostatic charge-discharge at 5 mA cm⁻², (e) areal specific capacitances versus discharge current density, and (f) EIS curves (inset shows the EIS curves at high frequency).

352 To further evaluate the possibility of the as-fabricated $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ core-shell NSAs for practical application,
 353 an asymmetric supercapacitor was assembled using $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs electrode as the anode and AC as the
 354 cathode. Figure 8a shows a schematic illusion of this ASC. Figure 8b shows CV curves of both AC and
 355 $\text{CoFe}_2\text{O}_4@\text{MnO}_2$ NSAs electrodes at a scan rate of 10 mV s^{-1} . The AC electrode revealed excellent electrochemical
 356 double layer capacitance performance between -1.0 and 0.0 V in view of the close-to-rectangular CV curve (black
 357 curve). In order to determine the working potential window of the full cell, we carried out the CV tests of the
 358 ASCs within different cell voltages varying from $0-1 \text{ V}$ to $0-1.6 \text{ V}$ (Figure 8c). The stable potential window for the
 359 assembled ASC can be extended to 1.6 V where the CV curve still maintained a rectangle-like shape. Therefore, the
 360 working potential window of $0-1.6 \text{ V}$ was chosen to investigate the electrochemical performances of
 361 $\text{CoFe}_2\text{O}_4@\text{MnO}_2 // \text{AC}$ ASC. With the increase of scan rates in CV tests, the CV profiles (Figure 8d) of the ASC
 362 still remained the rectangular-like shape without any redox peaks, indicating good charge-discharge property and
 363 rate capability of the ASC device. Figure 8e exhibits the GCD curves of the ASC device in a voltage window of
 364 $0-1.6 \text{ V}$ at different current densities. The charge curves of the ASC device were almost symmetric to its
 365 corresponding discharge counterpart, confirming the excellent capacitive character of $\text{CoFe}_2\text{O}_4@\text{MnO}_2 // \text{AC}$ ASC.
 366 The calculation of the specific capacitances of the ASC was based on the GCD tests. Figure 8f presents the mass
 367 and areal specific capacitances of $\text{CoFe}_2\text{O}_4@\text{MnO}_2 // \text{AC}$ ASC at different current densities. The specific
 368 capacitance of the full cell can achieve 103.86 F g^{-1} (0.883 F cm^{-2}) at 5 mA cm^{-2} , and still retained 43.12 F g^{-1}
 369 (0.367 F cm^{-2}) at a high current density of 51 mA cm^{-2} .

370 **Figure 8.** (a) Schematic illustration of the as-fabricated $\text{CoFe}_2\text{O}_4 @ \text{MnO}_2 // \text{AC}$ -ASC device. (b) Comparative CV
 371 curves of the activated carbon electrode and $\text{CoFe}_2\text{O}_4 @ \text{MnO}_2$ electrode at 10 mV s^{-1} . (c) CV curves at different
 372 cell voltages at a scan rate of 20 mV s^{-1} and (d) different scan rates for $\text{CoFe}_2\text{O}_4 @ \text{MnO}_2 // \text{AC}$ -ASC device. (e)

Galvanostatic charge-discharge curves at different current densities. (f) Specific capacitances of the CoFe₂O₄ @ MnO₂// AC-ASC device at different current densities.

Energy density and power density are two critical parameters to evaluate the electrochemical performances of supercapacitors. Figure 9a shows the Ragone plot of the CoFe₂O₄@MnO₂ //AC ASC based on GCD tests. The maximum energy density of the ASC was 37 W h kg⁻¹ at a power density of 470 W kg⁻¹ based on total mass of active materials. The energy density gradually decreased to 15.3 W h kg⁻¹ with the increase of power density from 470 W kg⁻¹ to 4800 W kg⁻¹. The energy densities and power densities of CoFe₂O₄@MnO₂ //AC ASC were compared to those of reported hybrid supercapacitors similarly based on MnO₂ and transition metal oxides (Figure 9a). Obviously, the energy density in this study was higher than that of Co₃O₄/MnO₂//MEGO (17.7 W h kg⁻¹),[48] GHCS//GHCS-MnO₂ (22.1 W h kg⁻¹),[49] FeCo₂O₄//AC (23 W h kg⁻¹)[26] and NiCo₂O₄/MnO₂//AG (9.4 W h kg⁻¹).[50] Significantly, the highest energy density of the CoFe₂O₄@MnO₂ //AC ASC exceeded those of most of the commercial cells such as Maxwell, Nesscap and ESMA and their power densities are comparable. Two CoFe₂O₄@MnO₂ //AC ASC devices were further assembled in series. After charged for 20s to about 3.2 V, the connected devices efficiently powered a 10-LEDs (red, 1.8 V, 20mA for each) (Figure 9b). More impressively, the device drove a motor (2.8V) more than 30 sec without the loss of rotational speed (Video in supplementary data). (Figure 9c). A long-term cycle stability of the CoFe₂O₄@MnO₂ //AC ASC was tested by repeating GCD tests at a high current density of 41 mA cm⁻² for 2250 cycles. As shown in Figure 10a, the specific capacitance of CoFe₂O₄@MnO₂ //AC ASC still remained 91.5% of its initial capacitance after cycling test. Figure S6 shows the GCD curves of typical first and last ten cycles and their shapes remained undistorted and almost symmetric. The EIS spectra of CoFe₂O₄@MnO₂ NSAs electrode after cycling test was recorded in order to investigate the change of interfacial electrochemical behaviors of the electrode after cycling test. As shown in Figure S7, the EIS spectra showed similar curve shape except for the change of R_{ct}. Based on this result, the conclusion was drawn that the decrease of capacitance after long-term cycle stability test was likely attributed to the increase of Faradaic charge transfer resistance. Figure S8 shows the SEM image of CoFe₂O₄@MnO₂ core-shell NSAs after 2250 cycling tests. The morphology of CoFe₂O₄@MnO₂ still maintained the core-shell nanosheet arrays and almost the same as that before cycling test (Figure S8a) except for a small collapse of vertically aligned MnO₂ nanosheets (Figure S8b), which further indicated its highly mechanical stability.

The high capacitance and excellent cycling stability of CoFe₂O₄@MnO₂ NSAs electrode can be attributed to the hierarchical core-shell nanostructure. Its mechanism was proposed in Figure 10b. The unique core-shell nanostructure has many apparent advantages as follows: (1) The mesoporous and highly conductive CoFe₂O₄ nanosheets grown directly on the Ni foam can provide an electron “superhighway” for charge storage and delivery, which neutralized the intrinsic poor conductivity of MnO₂. (2) Ultrathin MnO₂ nanosheets supported on CoFe₂O₄ nanosheets provided a large specific area facilitating a better electrode/electrolyte contact and an increased electroactive sites for redox reaction compared to the individual CoFe₂O₄ and MnO₂ nanosheets. (3) Both of the CoFe₂O₄ and MnO₂ were potential pseudocapacitive electrode materials, hence jointly contributed to the total capacitance of CoFe₂O₄@MnO₂ NSAs. (4) The good mechanical adhesion between CoFe₂O₄ and MnO₂ and electrical connection of the electrode materials to the Ni foam without any binder or conductive agents enhanced the long-term performance and improved the utilization of the hybrid electrode.

Figure 9. (a) Ragone plot of the $\text{CoFe}_2\text{O}_4 @ \text{MnO}_2//\text{AC-ASC}$ device. The values reported for others devices and some commercial supercapacitors are given here for a comparison. (b) A digital image showing the two ASC devices in series can lighten up ten red LED indicators. (c) A rotating motor derived by two supercapacitors in series.

Figure 10. (a) Cycling stability of $\text{CoFe}_2\text{O}_4 @ \text{MnO}_2//\text{AC-ASC}$ device at a current density of 41 mA cm^{-2} . (b) Schematic images of the charge storage advantage of this hierarchical core-shell nanostructure.

4. Conclusion

In conclusion, a facile, tunable hydrothermal method has been developed to fabricate hierarchical $\text{CoFe}_2\text{O}_4/\text{MnO}_2$ core-shell NSAs on Ni foam. The hybrid electrode exhibited a high specific capacitance of 3.59 F cm^{-2} at a current density of 2 mA cm^{-2} which was the currently highest among the reported CoFe_2O_4 -based materials and higher than most of MnO_2 -based composites. The excellent performance exhibited by $\text{CoFe}_2\text{O}_4/\text{MnO}_2$ NSAs was likely attributed to the synergetic effects between the properties of two components and their unique core-shell nanostructure. In addition, The assembled $\text{CoFe}_2\text{O}_4/\text{MnO}_2 // \text{AC}$ ASC achieved a high specific capacitance of 103.86 F g^{-1} (0.883 F cm^{-2}) at 5 mA cm^{-2} , and still retained 43.12 F g^{-1} (0.367 F cm^{-2}) at a high current density of 51 mA cm^{-2} . A maximum energy density was 37 W h kg^{-1} , and the cycling stability reached 91.4 % retention after 2250 cycles. Given the low cost, facile process and the excellent electrochemical performance, the as-fabricated $\text{CoFe}_2\text{O}_4/\text{MnO}_2$ NSAs electrode are expected to be a novel hybrid electrode material for the next generation energy storage devices.

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