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Structure-Engineered Core–Shell Ni–Co–O/NiCo-LDH Nanospheres as High-Performance Supercapacitor Electrodes

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Abstract: The development of a novel electrode material for energy storage devices is a grand challenge. Here, through a rational design of the structure, the electrochemical performance of the prepared sample could be improved while enhancing the conductivity and the synergistic effect of its components. Herein, we constructed a core–shell composite named Ni–Co–O/NiCo-LDH as the electrode material by a self-template method, which comprised hydrothermal and annealing steps. The as-prepared material exhibited a Chinese chestnut-like structure, and the core–shell structure was based on nanoneedles. The pseudocapacitance characteristics of the Ni–Co–O/NiCo-LDH electrode were significantly improved due to the good electrical conductivity of the core material and the unique core–shell structure, which led to a high electrochemical performance, reaching a high specific capacitance of 1434 F g^{−1} at the current density of 1 A g^{−1}. When assembled in a device with activated carbon (AC) as the negative electrode, the supercapacitor showed an energy density of 26 Wh kg^{−1} at a power density of 807 W kg^{−1}. Simultaneously, the device showed an excellent cycle stability, with 95% capacity retention after 3600 cycles at a current density of 6 A g^{−1}, which could largely widen the application of the supercapacitor.

Keywords: core–shell structure; pseudocapacitance; electrical conductivity; LDH; supercapacitor



Citation: Luo, Y.; Feng, X.; Wei, D.; Zhang, L.; Wang, Q.; Yang, F.; Qiu, S.; Xu, F.; Zou, Y.; Sun, L.; et al. Structure-Engineered Core–Shell Ni–Co–O/NiCo-LDH Nanospheres as High-Performance Supercapacitor Electrodes. *Coatings* **2023**, *13*, 353. <https://doi.org/10.3390/coatings13020353>

Academic Editor: Alicia de Andrés

Received: 21 December 2022

Revised: 14 January 2023

Accepted: 21 January 2023

Published: 3 February 2023



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1. Introduction

In recent decades, supercapacitors have drawn much attention as energy storage devices because of their great power density, long cycling life, fast charge–discharge rate, and excellent energy conversion efficiency [1–5]. As crucial components of a supercapacitor, carbon materials (such as AC, graphene, carbon nanotubes, etc.) are the most widely researched, commercialized, and technologically matured; they possess a large specific surface area, excellent chemical durability and good electrical conductivity [6,7]. However, the energy density of carbon materials is limited. Compared with electric double-layer carbon materials (EDLCs), pseudocapacitive materials usually deliver higher specific capacitance. For example, with a low cost and variable valences, transition metal oxide/hydroxide electrode materials possess higher specific capacitance through fast surface faradaic reactions [8].

Due to their high theoretical specific capacitance, nickel/cobalt-based materials have recently received extensive attention, especially their oxides and hydroxides. With the synergistic effect of Co and Ni, Co_xNi_yO(S) or their layered double hydroxides (LDHs), Co_xNi_yOH, behave remarkably in performance [9–13]. Though these samples showed high specific capacity and power density, their intrinsic properties differ. Compared with the LDHs, the Co_xNi_yO(S) oxidants showed better conductivity but lower specific

capacitance [14]. Hence, the balance between conductivity and capacity has become an important factor to consider. The LDHs are a kind of composites formed by Nickel or Cobalt hydroxides, with many internal heterojunctions, which could effectively enhance the capacitance. Wang et al. prepared a $\text{Ni}_{0.60}\text{Co}_{0.40}$ LDH electrode showing a high capacity of 5.15 C cm^{-2} at 5 mA cm^{-2} and holding 3.64 C cm^{-2} at 30 mA cm^{-2} . However, their electronic conductivity and ion transport were slow, leading to poor cycle life and rate performance [15].

Research has shown a rationally designed composite structure could effectively promote a synergistic effect between its multiple components, increasing the specific capacitance, improving the electron and ion transport characteristics in the capacitor electrode materials, and improving the cycle stability. Therefore, rational design has received extensive attention in constructing high-performance conventional supercapacitors in recent years. Therefore, to enhance the electrochemical performance of supercapacitors, a practical design is required. Selecting a high-conductivity substance for recombination became the first choice for improving conductivity. Ren et al. chose a high-conductivity substrate, 3D dendritic copper, to support the CoNi-LDH, obtaining an impressive specific capacitance [16]. With the same design, the substrate could be replaced with suitable carbon materials [17–19] or other conductive materials [20]. These strategies focus on enhancing the conductivity of CoNi-LDHs and achieving superior results, which supports the importance of this complex procedure [21]. Compared with single-component materials, multicomponent composite materials can compensate for the lack of a single material and fully utilize the benefits of each component and their potential synergistic effects.

General conductive substances such as carbon materials, conductive polymers, or metal elements exhibit low capacitance or poor electrochemical stability as single component of the electrode materials, which restricts the capacitance of the supercapacitor. Given the good chemical stability of oxidations, $\text{Co}_x\text{Ni}_y\text{O}(\text{S})$ possesses an outstanding conductivity with excellent electrochemical performance [22,23]. However, the capacitance would partly reduce after high-temperature calcination, which is caused by the reduction of mid-valence Co/Ni and the recrystallization process. Simultaneously, the performance of supercapacitors is related not only to the chemical composition of the electrode materials but also to their structures and morphologies [15,24]. Therefore, a novel structure with $\text{Co}_x\text{Ni}_y\text{O}$ as the core and NiCo-LDH as the shell was put forward, which improved the conductivity and specific capacitance.

In particular, adequately designed three-dimensional (3D) core-shell nanostructures can significantly expand the specific surface area and provide more surface redox sites and more channels for electrolytes to get through, thus allowing a fast ion/electron transport. This design is crucial for improving the electrochemical performance and structural stability [25–28]. Liu et al. fabricated $\text{MgCo}_2\text{O}_4@\text{CoFe-LDH}$ core-shell nanoarrays on Ni foams that exhibited an excellent specific capacitance of 903.15 C g^{-1} at 1 A g^{-1} , with high capacity retention and also low internal resistance (R_s) (0.75Ω) [29]. This core-shell strategy construction always relies on a hard template method which limits its applications and increases the weight of the electrode materials [30–32].

In this work, we constructed a Ni-Co-O/NiCo-LDH core-shell composite as the electrode material by a self-template method, which comprised hydrothermal and annealing steps. The proposed strategy includes both composition design and structure design. On the one hand, the electrical conductivity of the NiCo-LDH could be improved and led to achieving the enhancement of the specific capacitance; on the other hand, the core-shell structure could alleviate the volume change of the electrode during the working process and thus improve the rate performance and cyclability. Such a method of preparing electrode materials is facile, tunable, scalable, and cost-effective, which is crucial for applications in supercapacitors.

2. Experimental Sections

2.1. Sample Preparations

2.1.1. Preparation of the Chinese Chestnut-like NiCo-LDH and Ni-Co-O

The Chinese chestnut-like NiCo-LDH sample was synthesized by a modified method based on previous studies [33]. Typically, 2 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 4 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 20 mmol of urea were dissolved in 60 mL of distilled water and stirred. Then, we transferred the resulting solution into a Teflon-lined autoclave (120 °C for 5 h) and finally cooled it down to room temperature. The obtained product was washed thoroughly with ethanol and distilled water and put in a vacuum drier overnight (60 °C); it was named NiCo-LDH sample. Then, the as-prepared NiCo-LDH was calcined at 350 °C for 2 h in a nitrogen atmosphere at a 2 °C/min heating rate and then calcined in air at 350 °C for 2 h at a 2 °C/min heating rate; the resulting product was named the nickel-cobalt oxide (Ni-Co-O) sample.

2.1.2. Preparation of the Ni-Co-O/NiCo-LDH Core-Shell Composite

We placed 1 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 4 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 10 mmol of urea into 36 mL of deionized water and obtained a solution. We then added 0.1 g of the prepared Ni-Co-O and kept stirring for 30 min. We transferred the solution to a Teflon autoclave and placed it in an oven (120 °C for 5 h). The reaction product was washed thoroughly with deionized water and ethanol and dried (60 °C for 12 h). The resulting product was named Ni-Co-O/NiCo-LDH. After adding 0.05, 0.1, and 0.15 g of Ni-Co-O, the resulting composites were named Ni-Co-O/NiCo-LDH-0.05, Ni-Co-O/NiCo-LDH-0.1, and Ni-Co-O/NiCo-LDH-0.15, respectively.

2.2. Characterization

The microstructural characteristics of the samples were determined by scanning electron microscopy (SEM; Quanta 200, FEI, Hillsboro, OR, USA). At the same time, the atomic ratio and distribution of the elements contained in the samples were characterized by energy-dispersive X-ray spectroscopy (EDS). The microstructural features of the samples were further observed by transmission electron microscopy (TEM; Talos F200X, FEI, Hillsboro, OR, USA). Meanwhile, the exposed faces of the samples and their corresponding interplanar spacings were characterized by high-resolution transmission electron microscopy (HRTEM). The phase composition and crystal structure of the samples were identified by a powder X-ray diffractometer (XRD; Bruker-D8 Advance diffractometer, Billerica, MA, USA). The elemental composition of the samples and the corresponding elemental valence states were characterized by X-ray photoelectron spectroscopy (XPS; Thermo Scientific Escalab 250Xi, Thermo Fisher Scientific, Waltham, MA, USA). The nitrogen adsorption/desorption isotherms of the samples were obtained by Quantachrome Autosorb at −196 °C. The corresponding pore size distribution and Brunauer–Emmett–Teller (BET) specific surface area of the samples were also obtained.

2.3. Electrochemical Measurements

In this work, the electrode preparation was achieved by using a coating method to deposit the powder material. The active material and additives were mixed into a paste and coated on the surface of the current collector, then pressed to obtain an electrode after a drying procedure. Nickel foam was used as the current collector. The weight ratio of the active electrode material, acetylene black, and polytetrafluoroethylene was set at 8:1:1. The active material and additives were mixed evenly and ground to obtain a slurry, finally spreading the coatings on the Ni foam with a blade. The electrode preparation process finished after drying at 80 °C for 6 h. The mass of the produced electrode material was approximately 8–10 mg/cm².

Typically, the three-electrode system of a platinum foil as the counter electrode and a saturated calomel Hg/HgO electrode as the reference electrode was applied to test the electrochemical performance of the prepared samples. A 6 M KOH solution was used as

the electrolyte. In the two-electrode system test, the as-prepared positive electrode material, diaphragm, and negative electrode material (AC) were assembled in sequence to fabricate an asymmetric device and placed into the electrolyte for testing. In this work, the CHI760E electrochemical workstation was used to test the cyclic voltammetry (CV) and perform the galvanostatic charge–discharge test (GCD) and electrochemical impedance spectroscopy (EIS) of the electrodes and devices. The frequency range of ESI was from 0.01 Hz to 100 kHz, and the amplitude of the voltage was 5 mV.

3. Discussion and Results

Characterization

NiCo-LDH prepared by the traditional hydrothermal method exhibited a micron-level spherical structure with a size around 3–4 μm and presented a Chinese chestnut-like morphology comprising the building blocks of needle-like nanorods (Figure 1a,d). As shown in Figure S1, the NiCo-LDH samples appeared uniform, and the elements of Co, Ni, O were evenly dispersed, as shown by the results of EDS mapping. After calcination, the resulting oxide (Ni–Co–O) could maintain the chestnut-like microstructure (Figure 1b,e). Meanwhile, the size of the Ni–Co–O microspheres as well as the that of the nanoneedles became significantly smaller (Figure S2a). The EDS mapping results also indicated that the three elements were uniformly dispersed (Figure S2b–d). After the second hydrothermal process, the resulting Ni–Co–O/NiCo-LDH sample still maintained the Chinese chestnut-like microsphere structure, with an average particle size of 4 μm (Figure 1c,f). According to the EDS mapping, the distribution of Ni, Co, and O elements was uniform. (Figure 1g–j).

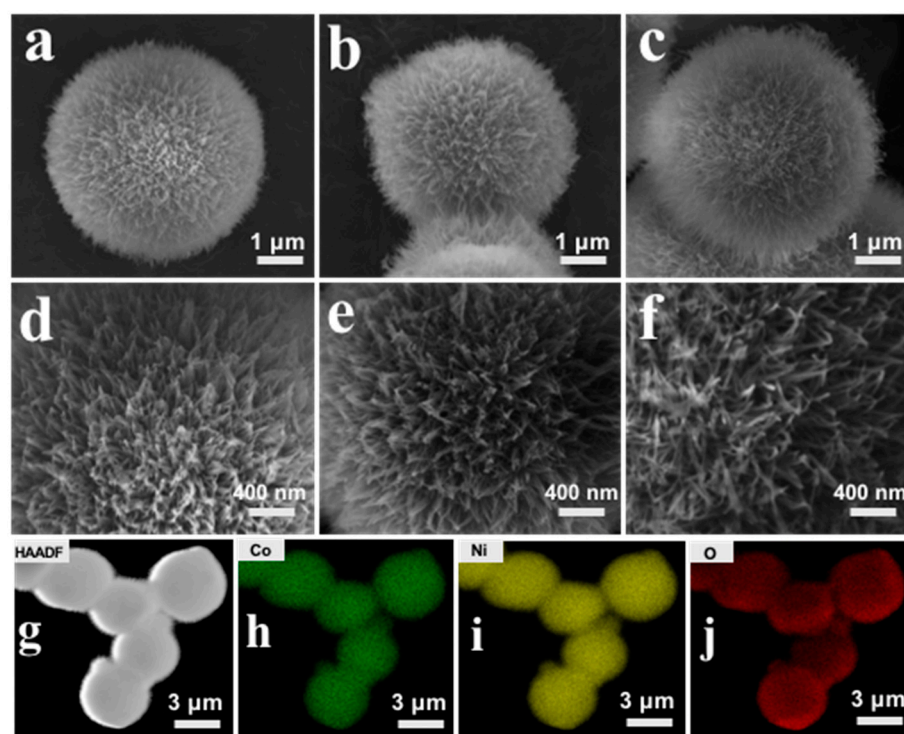


Figure 1. SEM images of (a,d) NiCo-LDH; (b,e) Ni–Co–O, and (c,f) the Ni–Co–O/NiCo-LDH composite, (g–j) EDS-HAADF of the Ni–Co–O/NiCo-LDH composite.

To further investigate the microstructure of the as-prepared samples, TEM characterization was conducted (Figure 2). The chestnut-like Ni–Co–O/NiCo-LDH appeared composed of many nanoneedles arranged in the radial direction of the microsphere (Figure 2a), which could provide a directional pathway for the electrons. These nanoneedles had an average length of over 500 nm and a diameter of ~ 20 nm (Figure 2b). In addition, the gap between adjacent nanoneedles appeared to facilitate the easy diffusion of the electrolyte, thus ensur-

ing that the nanoneedles could fully contact the electrolyte. In addition, the nanoneedles could provide more redox active sites in the discharge/charge process and thus improve the electrochemical performance. Figure 2c and d show that the lattice distance of 0.211 nm was in accordance with the (200) plane of NiCoO₂. Moreover, the lattice spacing of 0.248 nm agreed with the (111) plane of NiCoO₂ [34]. That indicated the successful combination of Ni–Co–O and NiCo-LDH.

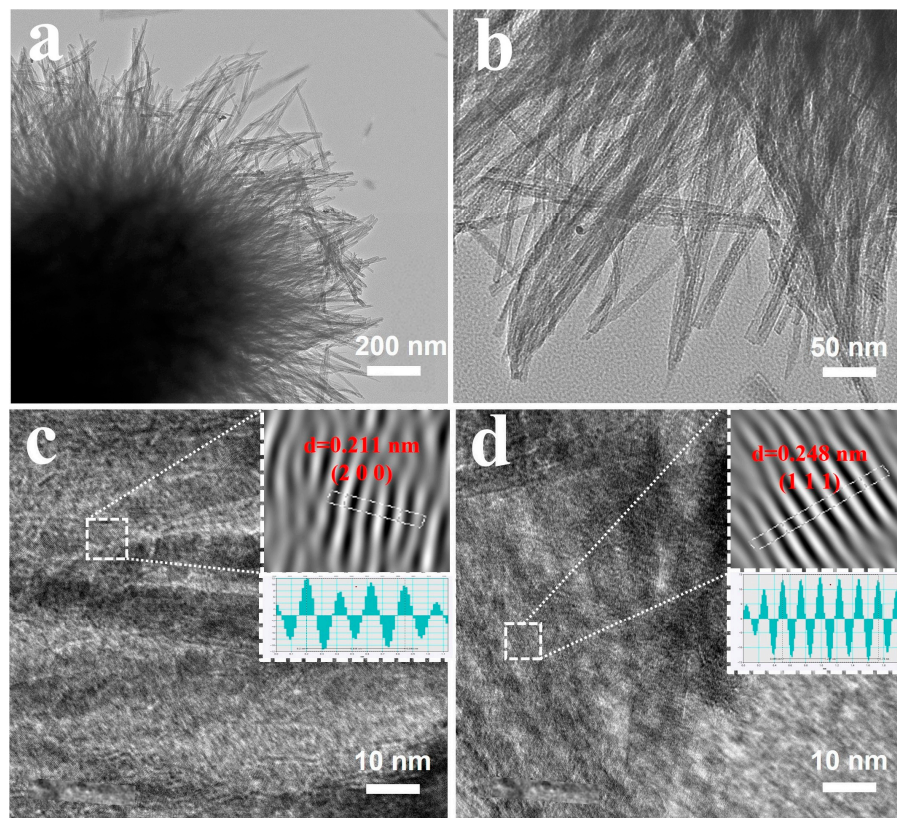


Figure 2. (HR)TEM of the Ni–Co–O/NiCo-LDH composite (a,b); the insets in (c) and (d) show the corresponding SAED patterns and inverse fast Fourier transform (FFT) images.

The XRD patterns of NiCo-LDH, Ni–Co–O, and Ni–Co–O/NiCo-LDH are shown in Figure S3. At 11.9°, 18°, 34°, and 59°, we observed characteristic XRD peaks belonging to the (003), (001), (012), and (110) crystal planes of the α -phase of the hydrotalcite-like LDH phase. The diffraction peaks with $2\theta = 37.3^\circ$, 43.3° , and 62.9° are related to the (111), (200), and (220) plane reflections of NiCoO₂. Diffraction peaks of NiCo-LDH and Ni–Co–O appeared in the XRD patterns of the composite, indicating that NiCo-LDH and Ni–Co–O were successfully compounded, which was consistent with the TEM results.

The surface elemental composition and chemical valence of the sample Ni–Co–O/NiCo-LDH were analyzed by XPS, as shown in Figure 3. The full spectrum demonstrated the presence of Ni, Co, and O in the sample (Figure 3a), which agreed with the EDS analysis. Figure 3b shows the high-resolution XPS spectrum of Ni 2p. The two characteristic peaks at the binding energies of 858.7 and 875.3 eV correspond to Ni 2p_{3/2} and Ni 2p_{1/2} of Ni²⁺, respectively [3]. The two spin-orbit double peaks at 797.4 eV and 782.5 eV were indexed to Co 2p_{1/2} and Co 2p_{3/2}, respectively (Figure 3c). This indicated the presence of Co²⁺ [16,33]. The fitting peaks at 780.8 eV and 795.9 eV correspond to Co³⁺. In Figure 3d, the peak of O1 could be related to H₂O molecules absorbed on the sample's surface [3]. The peaks of O2 and O3 matched with the binding energies of M–O–H and M–O–M, where M–O–H was attributed to the NiCo-LDH shell material, and M–O–M was indexed to the NiCoO₂ core material. From the above results, we could infer the successful synthesis of the Ni–Co–O/NiCo-LDH composite. Figures S4 and S5 show the XPS spectra of NiCo-LDH

and Ni–Co–O. No obvious differences were observed among the XPS results of the three samples, indicating that the chemical states of the elements in the three samples were the same.

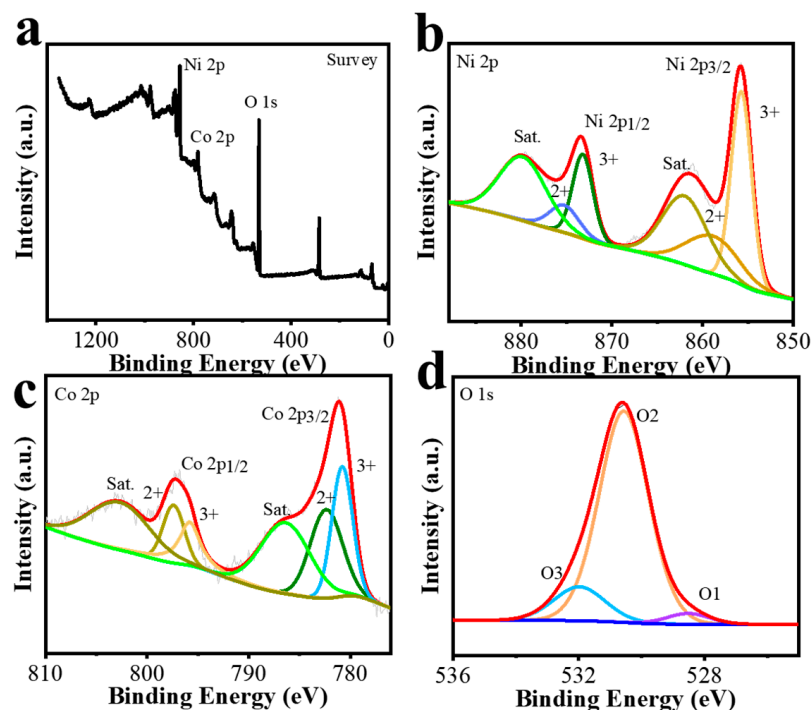


Figure 3. XPS survey spectrum (a), high-resolution spectra of Ni 2p (b), Co 2p (c), O 1s (d) in Ni–Co–O/NiCo-LDH.

The specific surface area and porosity of the as-prepared three samples were explored by N_2 physical adsorption/desorption isotherms, and the results are shown in Figure 4. The curves exhibited typical type IV adsorption–desorption isotherm loops, suggesting that there were mesopores in the microspheres (Figure 4a) [35]. The specific surface areas of the NiCo-LDH, Ni–Co–O, and Ni–Co–O/NiCo-LDH samples were 249.7, 130.1, and 221.6 $m^2 g^{-1}$, respectively. A high specific surface area can expose the active sites during the Faraday reaction. The pore size distribution of the Ni–Co–O/NiCo-LDH sample was narrow, and the diameter of the pores was in the range of 2–5 nm (Figure 4b), which helped reduce the electrolyte ion diffusion lengths and promoted a fast Faraday redox reaction.

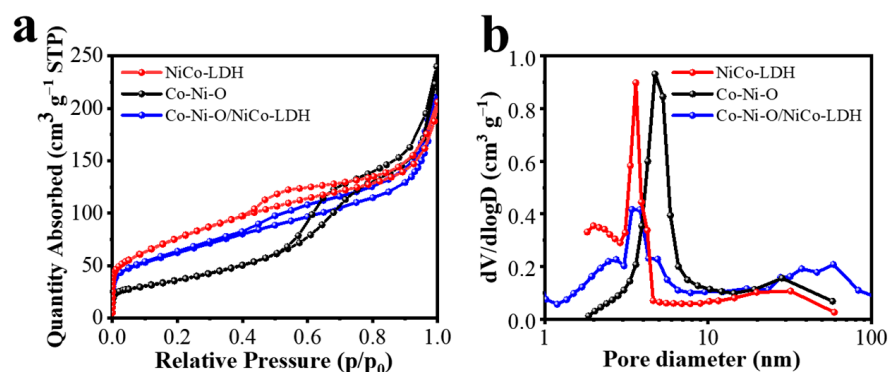


Figure 4. Nitrogen sorption isotherms (a) and (b) pore-size distributions in NiCo-LDH, Ni–Co–O, and the Ni–Co–O/NiCo-LDH composite.

To determine the best covering ratio of NiCo-LDH to Ni–Co–O, we optimized the ratio of the two components in the Ni–Co–O/NiCo-LDH composite. Figure S6 displays the CV

and GCD tests of Ni–Co–O/NiCo-LDH composites. When adding 0.1 g of Ni–Co–O, the composite showed the best electrochemical performance. The following electrochemical tests were based on this optimal sample.

Figure 5 shows the results of the double-electrode electrochemical performance test using the Ni–Co–O/NiCo-LDH electrode. Figure 5a shows the CV curves for the Ni–Co–O/NiCo-LDH core-shell electrode material under different scan rates. The CV curves show the capacitance characteristics and a pair of obvious redox peaks, indicating the pseudocapacitive energy storage mechanism. As the scan rate increased from 5 mV s^{-1} to 100 mV s^{-1} , the CV curve's shape did not change significantly. In contrast, the area increased gradually, and the peak current also increased, which suggested the electrochemical reversibility of the electrode material was good.

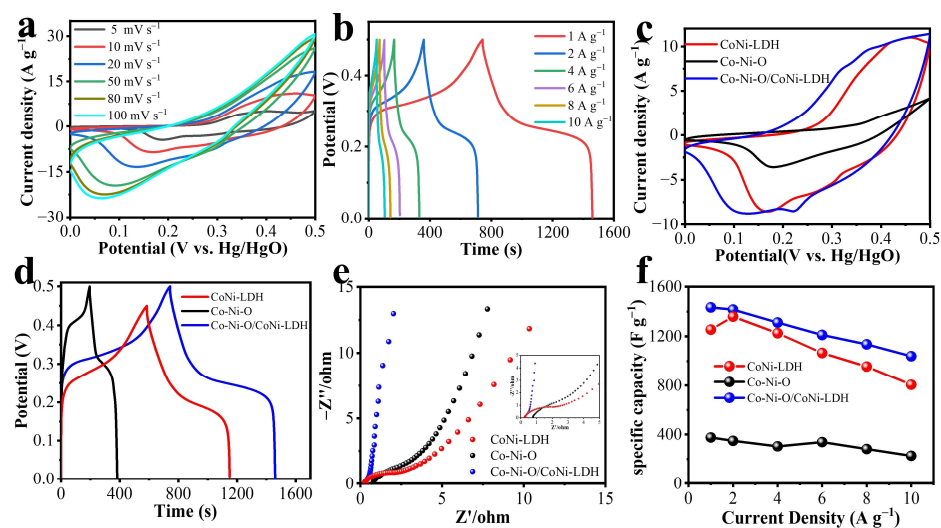


Figure 5. (a) CV and (b) GCD curves of the Ni–Co–O/NiCo-LDH composite; (c) CV curves of NiCo-LDH, Ni–Co–O, and the Ni–Co–O/NiCo-LDH composite at a scanning rate of 10 mV s^{-1} ; (d) GCD curves of NiCo-LDH, Ni–Co–O, and the Ni–Co–O/NiCo-LDH composite at a current density of 1 A g^{-1} ; (e) EIS plots of NiCo-LDH, Ni–Co–O, and the Ni–Co–O/NiCo-LDH composite; (f) specific capacitance plots of NiCo-LDH, Ni–Co–O, and the Ni–Co–O/NiCo-LDH composite at different current densities.

To explore the origin of the capacitive behavior, an analysis of the contribution of EDLC and pseudo-capacitance (PC) towards the overall specific capacitance was conducted by the Trasatti's method. In the Trasatti's method, the surface-controlled capacities are divided into "inner" and "outer" portions. Specifically, "inner" surfaces are the regions with difficult access, while "outer" surfaces refer to surfaces that ions directly come in contact with [36,37]. Figure S7 exhibits the linear fit of capacity (q) vs. the reciprocal of the square root of the scan rate ($v^{-1/2}$) and q^{-1} vs. $v^{1/2}$ for the sample Ni–Co–O/NiCo-LDH. A ohmic drop of the intrinsic resistance was responsible for the non-linear behavior of the graphs [38]. After the evaluation, the sample Ni–Co–O/NiCo-LDH exhibited 5.3% and 94.7% of the capacity, originating from the EDLC and PC contributions, respectively. The high proportion of PC indicated that the core-shell composition provided the main pseudo-capacitive properties, while the microstructure of the chestnut-like structure provided part of the electric double-layer properties, which jointly promoted the high electrochemical performance of the composite.

Figure 5b shows the GCD curves of the Ni–Co–O/NiCo-LDH core-shell electrode material at various current densities. It shows apparent charge-discharge platforms that further proved the pseudocapacitive energy storage mechanism [39]. According to the GCD curves, the specific capacitance of the Ni–Co–O/NiCo-LDH core-shell electrode at different current densities could be calculated. It exhibited specific capacitance values of

1434, 1416, 1312, 1212, 1136, and 1040 F g⁻¹ at the current densities of 1, 2, 4, 6, 8, and 10 A g⁻¹, respectively.

The CV and GCD of the individual components NiCo-LDH and Ni-Co-O were also tested (Figures S8 and S9), which identified the excellent symmetry and high capacity of Ni-Co-O/NiCo-LDH. The CV curves of the as-prepared NiCo-LDH, Ni-Co-O, and Ni-Co-O/NiCo-LDH at a scan rate of 10 mV s⁻¹ were compared (Figure 5c). The CV curves of the three electrode materials showed the capacitance characteristics and obvious redox peaks. As expected, when the NiCo-LDH and Ni-Co-O were combined to form a core-shell structure, the CV curve area significantly increased, and the peak current also increased compared with those of NiCo-LDH or Ni-Co-O. In addition, two distinct redox peaks could be observed, demonstrating an electrochemical reaction behavior in the presence of Faradaic processes. Figure 5d shows the GCD curves of the as-prepared NiCo-LDH, Ni-Co-O, and Ni-Co-O/NiCo-LDH samples at the current density of 1 A g⁻¹. The GCD curves of the three electrodes showed clear charge-discharge platforms, which also proved the pseudocapacitive energy storage mechanism; the discharging time increased significantly after the core-shell structure formed. Compared with Ni-Co-O, the broadened potential window of Ni-Co-O/NiCo-LDH further indicated that the composite of this core-shell structure would successfully reduce the polarization and enhance the specific capacitance (Figures S10 and S11).

Figure 5e shows the EIS results of the three electrode materials. In the low-frequency region, the linear slope of the Ni-Co-O/NiCo-LDH electrode material is larger than that of the two single-component electrode materials, which indicated that the composite had lower internal impedance, showing a faster diffusion of ions, which allowed a faster and complete contact between the electrolyte ions and the electrode materials. In the high-frequency region, the semicircle of the Ni-Co-O/NiCo-LDH electrode material becomes smaller, indicating that the charge transfer resistance was significantly reduced, which is beneficial to the rapid transfer of electrons, consequently promoting the rate performance of the electrode. The EIS data were fitted to the equivalent circuit shown in inset of Figure S12 [40]. The electrochemical parameters of the series resistance (R_s) and the charge transfer resistance (R_{ct}) were obtained as shown in Table S1. Ni-Co-O/NiCo-LDH had a lower R_{ct} than the other two materials, suggesting fast kinetics in the discharge/charge process [41,42]. This result further proved that due to the construction of the composite material, the electron transport rate of the electrode was improved to a certain extent.

Figure 5f displays the rate capability of the three electrode materials. The specific capacitance value of the Ni-Co-O/NiCo-LDH electrode material was higher than those of the single components at each current density, and the rate performance was also improved. Especially at high rates, e.g., at a current density of 10 A g⁻¹, the highest specific capacitance value could reach 1040 F g⁻¹, much higher than the specific capacitance value of the NiCo-LDH (806 F g⁻¹) and Ni-Co-O electrodes (226 F g⁻¹). With the construction of the core-shell structure, the specific capacitance of the electrode material significantly increased at any current density. This was due to the synergistic effect of NiCo-LDH and Ni-Co-O, while the high conductivity of Ni-Co-O restrained the polarization of the composite. Typically, redox reactions are challenging to occur in the core part of a core-shell structure, and most of them occur at the surface. In the present work, the core-shell structure formed based on the nanoneedles' structure. Such unique microstructure is very thin, and the core material is more accessible to the electrolyte, which allows for a faster electron transport and further increases the specific capacitance and reduces the polarization of the electrode material. Moreover, the specific surface area, which showed more electroactive sites, also plays a vital role. Hence, the above advantages provided the as-prepared Ni-Co-O/NiCo-LDH core-shell structure with an excellent electrochemical performance.

To evaluate further the practical possibility of preparing electrode materials, an asymmetric supercapacitor was fabricated, using the prepared Ni-Co-O/NiCo-LDH core-shell structure electrode as the positive electrode, AC as the negative electrode, and 6 mol L⁻¹ of KOH as the electrolyte. Figure S13 shows the CV curves of the Ni-Co-O/NiCo-LDH

electrodes (0–0.5 V) and AC/NF electrodes (−1.0~0 V) at a scan rate of 10 mV s^{-1} . The CV curve of the AC/NF negative electrode showed a rectangular shape, indicating that this AC electrode is an ideal double-layer capacitor based on the rapid desorption/adsorption of the electrolyte ions. According to the previous experimental results, the operating voltage windows of the Ni–Co–O/NiCo-LDH electrode and the AC negative electrode were 0–0.5 V and −1~0 V, respectively. Therefore, the operating voltage range of the assembled supercapacitor was 0–1.5 V. Figure 6a shows the CV curves of the asymmetric supercapacitor in various voltage ranges (from 0–1.2 V to 0–1.8 V) at a scan rate of 10 mV s^{-1} . When the voltage range increased from 1.2 V to 1.6 V, the shape of the CV curve of the asymmetric supercapacitor did not change. Therefore, the asymmetric supercapacitor could operate stably in the voltage range of 1.6 V. Figure 6b displays that the assembled asymmetric supercapacitor had an electric double layer and pseudocapacitive behavior characteristics. As the scan rate increased, the area of the CV curve gradually increased, and the shape of the CV curve changed only slightly, which showed its excellent Faraday reaction process and rate performance. Figure 6c shows the GCD curves of asymmetric supercapacitors at different current densities. According to the GCD curve, we could calculate the specific capacitance value of the asymmetric capacitor. The calculation result is shown in Figure 6d. At 1 A g^{-1} current density, the specific capacitance of the asymmetric capacitor could reach 72.3 F g^{-1} ; when the current density increased to 10 A g^{-1} , the specific capacitance of the asymmetric capacitor was 30.6 F g^{-1} , displaying a good rate performance.

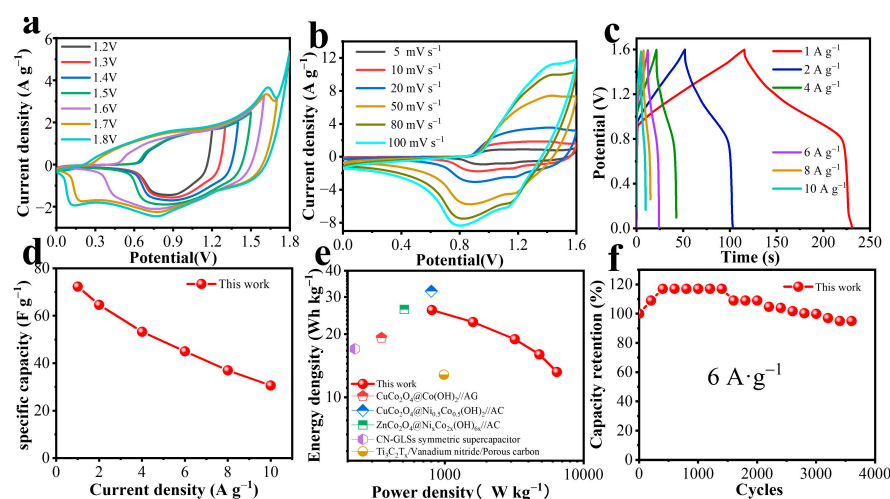


Figure 6. (a) CV curves of the Ni–Co–O/NiCo-LDH//AC electrode collected over various potential windows at 10 mV s^{-1} , (b) CV curves of the asymmetry device at different scan rates ranging from 5 to 100 mV s^{-1} , (c) GCD at various current densities from 0 to 1.6 V ; (d) specific capacitance plots of the asymmetry device at different current densities; (e) Ragone plot illustrating energy and power densities of the Ni–Co–O/NiCo-LDH//AC device and other electrochemical devices; (f) cycling life of the device with 3600 cycles at 6 A g^{-1} .

The calculated energy density and power density of the assembled asymmetric supercapacitor are shown in the Ragone diagram (Figure 6e). When the power density was 807 W kg^{-1} , the energy density of the asymmetric capacitor could reach 26 Wh kg^{-1} . When the power density increased to 6422 W kg^{-1} , the energy density could still be maintained at 13.2 Wh kg^{-1} . The figure also shows a comparison between our results and others in the literature, as reported in Table S2 [39,43–47]. It can be seen that the performance of the asymmetric supercapacitor assembled in this work was relatively excellent. Meanwhile, the device exhibited lower impedance, which can accelerate electron transfer and reduce internal energy dissipation (Figure S14).

In addition, to explore the stability of this supercapacitor, 3600 discharge and charge tests were conducted on the asymmetric capacitor under a current density of 6 A g^{-1} .

(Figure 6f). After 3600 cycles, the asymmetric capacitor retained 95% of the original capacity, indicating that the asymmetric capacitor had a good cycle performance.

4. Conclusions

In conclusion, a Ni–Co–O/NiCo-LDH core–shell composite was designed and successfully synthesized by the self-template method. The Ni–Co–O/NiCo-LDH core–shell composite showed a Chinese chestnut-like morphology composed of nanoneedles. When used as the electrode material of supercapacitors, the Ni–Co–O/NiCo-LDH composite exhibited high specific capacitance and good rate performance. Several reasons may explain this good electrochemical performance. First, the electrical conductivity of NiCo-LDH improved after combining with Ni–Co–O, which also improved its specific capacitance. In addition, the core–shell structure composed of many nanoneedles could provide a directional pathway for the electrons, which promoted the electron transfer. Moreover, the Ni–Co–O/NiCo-LDH composite has a high specific surface, which helped expose more active redox sites. The electrode material prepared in this work not only has excellent electrochemical performance, but also has potential application in supercapacitors due to its simple preparation method and low cost.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings13020353/s1>, Figure S1: SEM and EDS images of NiCo-LDH; Figure S2: SEM and EDS images of Ni–Co–O; Figure S3: XRD patterns of NiCo-LDH, Ni–Co–O, and the Ni–Co–O/NiCo-LDH composite; Figure S4: XPS survey spectrum (a), high-resolution spectra of Ni 2p (b), Co 2p (c), O 1s (d) for NiCo-LDH; Figure S5: XPS survey spectrum (a), high-resolution spectra of Ni 2p (b), Co 2p (c), O 1s (d) for Ni–Co–O; Figure S6: CV and GCD curves of composites obtained from different ratios of the two components of the Ni–Co–O/NiCo-LDH composite; Figure S7: (a) linear fit of the capacity (q) vs. the reciprocal of the square root of the scan rate ($v^{-1/2}$) of Ni–Co–O/NiCo-LDH, (d) linear fit of the reciprocal of capacity (q^{-1}) vs. the square root of the scan rate ($v^{1/2}$) of Ni–Co–O/NiCo-LDH. Figure S8: (a) CV and (b) GCD curves for NiCo-LDH; Figure S9: (a) CV and (b) GCD curves for Ni–Co–O; Figure S10: (a) CV and (b) GCD curves for the Ni–Co–O/NiCo-LDH composite under different potential windows; Figure S11: (a) CV and (b) GCD curves of Ni–Co–O under different potential windows; Figure S12: The equivalent circuit of EIS data fitting; Figure S13: CV curves of Ni–Co–O/NiCo-LDH electrodes (0–0.5 V) and AC/NF electrodes (−1.0–0 V) at a scan rate of 10 mV s^{−1}; Figure S14: EIS of the Ni–Co–O/NiCo-LDH//AC device. Table S1: R_{ct} and R_s of different samples. Table S2: Comparison of the electrochemical properties of the NiCo-LDH/Ni-Co-O electrode and other electrodes reported in the literature.

Author Contributions: The manuscript was written with the contributions of all authors. Conceptualization, Y.L. and Q.W.; methodology, X.F., Y.L., Q.W. and H.C.; investigation, X.F., D.W. and L.Z.; funding acquisition, Y.L., Q.W., H.C., S.Q. and L.S.; writing—original draft preparation, Y.L. and Q.W.; writing—review and editing, Y.L., F.Y., S.Q., Q.W., H.C. and L.S.; data curation, X.F., D.W. and L.Z.; supervision, S.Q., F.X. and Y.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of Guangxi (2022GXNSFBA035610 and 2022GXNSFBA035632); the National Natural Science Foundation of China (52201245, 52201206, 22179026, 21965007, and 52161035); the China Postdoctoral Science Foundation (2021M693810); the Talent Special Project of Guangxi Province (AD21220115); the Scientific Research and Technology Development Program of Guilin (20210102-4, 20210216-1); the Research Program of Basic Research Capabilities Improvement for Young and Middle-Aged Teachers of Universities in Guangxi (2021KY0205 and 2021KY0199); the Research program of the Guangxi Key Lab of Wireless Wideband Communication and Signal Processing (GXKL06200124); the Scientific Research Program Funded by the Shaanxi Provincial Education Department (21JK0636).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are openly available via MDPI.

Acknowledgments: We especially thank the China Postdoctoral Foundation, Guangxi Postdoctoral Foundation, Guangxi Bagui Scholars, Lijiang Scholars.

Conflicts of Interest: The authors declare no conflict of interest.

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