

Research Progress of NiCo-Based Materials in High-Performance Supercapacitors

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Abstract: Nickel-cobalt (NiCo)-based materials have emerged as promising electrode candidates for advanced supercapacitors (SCs) owing to their multiple valence states, abundant redox-active sites, and tunable structural characteristics. However, their practical deployment is still constrained by challenges including limited electrical conductivity, structural instability during repeated redox cycling, and inefficient ion/electron transport, depending on their composition and electrode architecture. To address these limitations, recent research has increasingly focused on multidimensional structural and compositional engineering. This review systematically summarizes recent advancements in NiCo-based electrodes, including morphology control, self-supporting electrode construction, MOF-assisted derivatization, and functional coating strategies. Specifically, precise morphology control through synthetic parameters, ligand, and template regulation can increase active-site accessibility and facilitate ion transport. Integrating tailored NiCo-based structures onto conductive substrates to form binder-free, self-supporting electrodes reduces interfacial resistance and provides robust electrode architectures. In addition, MOFs serve as versatile structural platforms and precursors for deriving NiCo-based oxides, sulfides, phosphides, and layered double hydroxides (LDHs), which can improve electrical conductivity and structural stability while retaining favorable porous features. Furthermore, integrating NiCo-based materials with functional components such as carbon materials, MXenes, and transition-metal compounds provides additional opportunities to regulate interfacial charge transfer and structural stability through multicomponent interactions. Finally, this review discusses current challenges and future perspectives, including interfacial evolution revealed by in-situ/operando characterization, rational material design assisted by theoretical calculations and machine learning, and the practical development of high-performance NiCo-based supercapacitor electrodes.

Keywords: supercapacitors; NiCo-based materials; morphology control; self-supporting electrodes; MOF-derivatives; functional coatings



1. Introduction

Against the backdrop of global climate governance and low-carbon transition, renewable energy sources such as wind and photovoltaic power have experienced large-scale development. However, their inherent intermittency and fluctuation cause supply-demand mismatches, while traditional fossil fuels face constraints from geopolitical factors and strict carbon emission regulations. Consequently, high-efficiency electrochemical energy storage technologies have become a cornerstone of energy system transformation, driving an urgent demand for advanced energy storage devices [1]. Compared to traditional batteries, which suffer from sluggish reaction kinetics, structural degradation, and temperature sensitivity, SCs exhibit superior power density, long cycle life, and wide temperature adaptability. The performance of supercapacitors (SCs) is fundamentally governed by the electrode materials. Conventional carbon-based materials deliver low specific capacitance, while single nickel/cobalt-based materials lack sufficient conductivity and structural stability [2]. By contrast, NiCo-based materials, leveraging bimetallic synergies, offer abundant redox sites, multiple valence states, and tunable microstructures, emerging as highly promising electrode candidates. Nevertheless, NiCo-based materials still face critical bottlenecks: NiCo-MOFs inherently suffer from poor electrical conductivity due to insulating organic ligands, while both MOFs and NiCo-layered double hydroxides (LDHs) are plagued by severe structural instability caused by volume expansion and structural collapse during long-term Faradaic cycling [3,4].

Numerous efforts have been made to address these challenges, including morphology regulation, the construction of self-supporting systems, the preparation of MOF derivatives, and the fabrication of functional coatings. While current research on NiCo-based electrode materials has made significant progress, most studies tend to focus on single-dimensional modifications—such as morphology or derivation alone [5–8]. These aspects have rarely been systematically integrated and discussed in a coordinated manner. Since the energy storage performance of these materials is synergistically determined by morphology, structure, composition, and interfacial properties, a single optimization strategy is insufficient to fully unlock their potential. Therefore, this review systematically investigates the design strategies, coordination mechanisms, and performance correlations from morphology regulation, self-supporting systems, derivatives, and composite systems, in order to provide comprehensive references for the development of high-performance SC electrodes.

The morphology of SC electrode materials serves as the foundation of their performance, determining the abundance of active sites and the efficiency of ion transport, while providing microstructural support for subsequent self-supported construction, derivative modification, and composite optimization. By adjusting metal ion ratios, selecting different ligands, or employing sacrificial template methods, the microscopic morphology of MOFs can be precisely controlled. This enables the formation of porous nanosheets or hollow nanocages, which significantly increase the specific surface area and accelerate ion diffusion kinetics. For instance, Sun et al. synthesized amino-functionalized NiCo-MOF powders and precisely controlled various morphologies by adjusting the solvent composition, achieving an optimized specific capacitance of 1126.7 F g^{-1} at 0.5 A g^{-1} [9]. However, conventional powder-like materials require insulating binders that inevitably cause material detachment and a reduction in energy density. This issue can be circumvented by constructing binder-free self-supporting electrodes. For instance, Jia et al. fabricated NiCo-MOF nanosheets on nickel foam (NF) via in-situ electrodeposition and soaking, yielding a superior capacitance of 1289 F g^{-1} at 0.5 A g^{-1} [10]. Nevertheless, its moderate retention of 71.4% after 6000 cycles exposes the inherent structural fragility of pristine MOFs during repeated cycling. To alleviate the limitations associated with structural instability and poor conductivity, converting MOF precursors into inorganic derivatives (e.g., oxides, sulfides, or LDHs) provides an effective strategy for improving electrical transport and structural robustness while retaining, to varying degrees, the hierarchical porous features of the precursor. For example, Bhoite et al. derived a NiCo_2O_4 thin-film electrode via thermal annealing, achieving 1251 F g^{-1} at 0.5 mA cm^{-2} with a robust 93.55% capacitance retention over 10,000 cycles [11]. Finally, to mitigate the volume expansion and kinetic limitations of single-component derivatives, integrating heterostructures with functional materials (e.g., carbon, MXenes, metal compounds) has emerged. This strategy exploits multi-component synergy to optimize charge distribution and buffer volume changes, boosting both reaction kinetics and long-term stability [12].

Based on the aforementioned research routes, this paper systematically reviews the latest advancements of NiCo-based electrode materials in high-performance SCs. The core content focuses on morphology engineering, self-supporting electrode construction, MOF derivatization, and composite structure design (Figure 1), aiming to deeply explore the electrochemical mechanisms behind performance enhancement and the intrinsic structure-activity relationships. Finally, we analyze the current challenges faced by NiCo-based materials and look forward to the development directions of NiCo-based materials, providing a helpful theoretical foundation for the rational design of NiCo-based electrodes for next-generation SC materials.

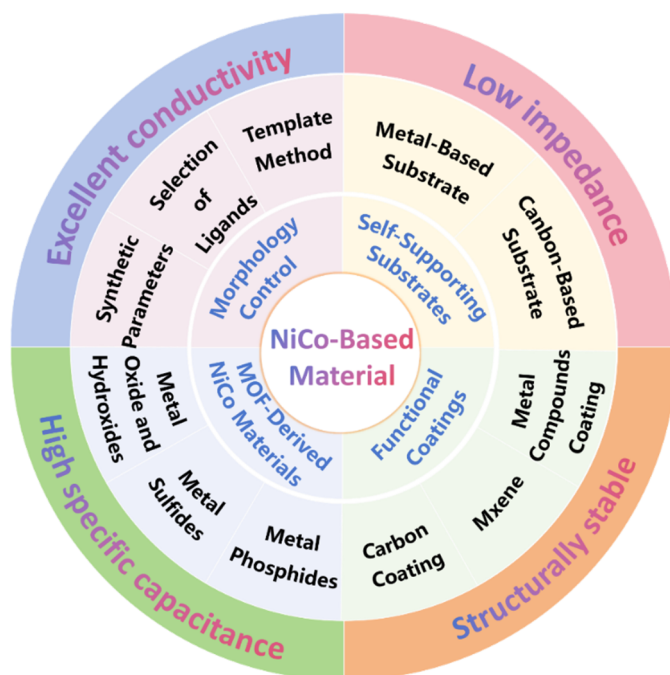


Figure 1. Major modified strategies for NiCo-based materials in SCs.

2. Morphology Control for NiCo-Based Materials

Morphology regulation is essential for tailoring the electrochemical performance of NiCo-based electrode materials, as it directly determines exposed active sites, ion transport kinetics, and structural stability. This chapter systematically elaborates on the morphology control of NiCo-based materials from two core aspects. The first focuses on synthetic parameter regulation, including the modulation of Ni/Co molar ratio, solvent composition, solvothermal temperature and duration, as well as rational ligand selection. The second part is MOF template engineering, exploring how different templates guide the construction of hierarchical microstructures.

2.1. Regulation of Synthetic Parameters for NiCo-Based Materials

Ni and Co play distinct yet highly complementary roles in NiCo-based materials for SCs. Ni, possessing rich mixed valence states ($\text{Ni}^{2+}/\text{Ni}^{3+}$), primarily provides dense faradaic active sites to contribute high pseudocapacitance, whereas the introduction of Co ($\text{Co}^{2+}/\text{Co}^{3+}$) significantly enhances the intrinsic electrical conductivity and stabilizes the structural framework. However, the combination of these two metals is not a simple physical superposition, but rather a profound competition and synergy at the atomic level. Extensive research has demonstrated that the initial molar ratio of $\text{Ni}^{2+}/\text{Co}^{2+}$ in the precursor solution directly dictates the crystal growth trajectory and the final morphology. A higher concentration of Ni^{2+} tends to drive the lateral expansion of 2D nanosheets, optimizing the microstructure. Meanwhile, increasing the Co^{2+} proportion induces the 1D anisotropic growth of nanoneedles or nanorods, resulting in a stable framework [13–15]. For instance, Fan et al. demonstrated that the Ni/Co ratio played a crucial role in determining the crystal growth behavior of Ni-Co binary hydroxide electrodes. By adjusting the different initial $\text{Ni}^{2+}/\text{Co}^{2+}$ molar ratios (9:1, 7:3, 5:5, 3:7, and 1:9), the morphology of Ni-Co hydroxide evolved from nanosheets to integrated nanosheet/nanowire architectures and finally to nanowires (Figure 2a–f). This morphological evolution was attributed to the competitive coordination between Ni and Co ions during hydroxide formation, which affected the nucleation and growth processes. Among these structures, the optimized $\text{Ni}_{0.5}\text{Co}_{0.5}(\text{OH})_2$ electrode with an integrated nanosheet/nanowire architecture exhibited abundant accessible active sites and shortened ion/electron transport pathways, delivering a high specific capacitance of 2807 F g^{-1} at 1 A g^{-1} while retaining 80.2% of its initial capacitance after 2000 cycles (Figure 2g) [16]. Various studies have shown that by adjusting the Ni/Co metal ion ratio, NiCo-based materials with different morphologies such as nanosheets, dandelion-like, and nanospike-like can be controllably synthesized [8,17,18]. Changing the ratio of metal ions can effectively adjust the electronic structure and electrical conductivity, thus optimizing the specific surface area and ion transfer paths.

Besides regulating the Ni/Co metal-ion ratio, the volumetric ratio of mixed solvents (e.g., water and ethanol) serves as a critical parameter for tuning the micromorphology of NiCo-based materials. While water provides an environment for rapid hydrolysis, the introduction of organic solvents significantly alters the dielectric constant

and solubility of the system, thereby retarding the nucleation rate and directing crystal growth. Extensive studies have demonstrated that optimizing the water/alcohol ratio effectively prevents the disordered agglomeration of nanocrystals, inducing the self-assembly of materials into mesoporous microspheres or hierarchical array structures, ultimately boosting the energy storage kinetics of SCs [19–21]. Ramulu et al. successfully prepared NiCo-MOF materials with controllable morphology by adjusting the proportion of deionized water (DIW)/dimethylformamide (DMF)/ethylene glycol (EG) ternary mixed solvent. The appropriate solvent polarity and steric hindrance effect can induce directional crystal growth. When the volumetric ratio of DIW/DMF/EG is optimized to 2:1:1, the NiCo-MOF sample forms an accordion-like multi-level porous structure, which has high-porosity channels and an enlarged electrochemically active surface. Benefiting from this optimized morphology, the NiCo-MOF electrode exhibited an areal capacity of $2621 \mu\text{Ah cm}^{-2}$ at 7 mA cm^{-2} and maintained a rate capability of 82.5% at 40 mA cm^{-2} . Moreover, an aqueous HSC assembled using the optimized NiCo-MOF as the positive electrode and activated carbon-coated Ni foam as the negative electrode was evaluated over 120,000 charge-discharge cycles, providing a representative example of long-term device-level stability [22].

Besides, the temperature and holding time settings for the solvothermal process are critical parameters that directly influence the crystallization process and ultimately determine the electrochemical performance of the NiCo-MOF. Meng et al. utilized graphene nanosheets (GNS) as the supporting material for in-situ growth of flower-shaped NiCo-MOFs composites (NiCo-MOFs/GNS) by employing a self-assembly solvothermal method. Appropriate temperature conditions (180°C , 8 h) can promote the self-assembly of NiCo-MOF nanosheets into a flower-like structure, avoiding incomplete growth due to insufficient conditions or agglomeration caused by excessive conditions. The flower-like structure provides rapid penetration and transfer channels for OH^- , thereby endowing the corresponding electrodes with an excellent specific capacity of 1080.0 C g^{-1} at 1 A g^{-1} [23]. By precisely regulating the temperature or time of solvothermal reactions, a series of NiCo-based SC electrode materials with specific micro-morphologies (such as 1D nanoneedle arrays, 2D nanosheets, 3D flower/urchin-like microspheres) have been successfully fabricated. Such microstructural engineering based on thermodynamic and kinetic conditions greatly expands the solid-liquid interfacial area to promote the rapid physical adsorption of electrolyte ions, thereby significantly enhancing the electric double-layer capacitance. Simultaneously, the shortened ion-diffusion pathways and exposed active sites strongly trigger the bulk Faradaic redox reactions, maximizing the pseudocapacitance [24–27].

The optimization of synthesis parameters lays the foundation for morphology, while organic ligands, as the framework of MOF structures, have a stronger guiding effect on morphology due to their chemical characteristics. The ligand coordination environment acts as a key factor to dominate the crystal orientation and self-assembly of NiCo-MOF, which can achieve abundant morphological evolution. The orientation of crystal nucleation and the self-assembly process are regulated by changing the coordination mode and bond strength with metal ions, thereby determining the micro-morphology and structural dimensions of the NiCo-MOF materials.

Compared to the physicochemical regulation that relies solely on solvothermal kinetics and metal ion ratios to induce crystal growth, the rational selection of organic ligands provides an alternative chemical strategy for NiCo-MOF to precisely customize multidimensional morphologies and pore networks bottom-up at the molecular level. Sahoo et al. employed the solvothermal method, using terephthalic acid (BDC), 2-methylimidazole (2-MeIm), and trimesic acid (BTC) as monoligands to synthesize NiCo-MOFs with diverse morphologies. Different ligands determine the formation of different structures; typically, BDC directed rectangular-like nanosheets, 2-MeIm directed petal-like nanosheets, and BTC directed nanosheet-assembled flower-like spheres. The study demonstrated that the number of coordination sites of the ligands and the strength of the metal-ligand interaction determined the crystal growth orientation. Thanks to the structural advantages, the BTC-based NiCo-MOF electrode achieved a capacity of 1471.4 C g^{-1} at 1 A g^{-1} , and a 91.4% capacitance retention rate after 4000 cycles at 10 A g^{-1} . The assembled asymmetric supercapacitor (ASC) achieved a high-energy density of 78.1 Wh kg^{-1} , significantly superior to the electrodes prepared by the other two ligands [28].

Compared with the traditional single-ligand coordination mode, dual-ligand cooperative coordination for NiCo-MOF can realize precise structure regulation and electrochemical property improvements through the complementary spatial configuration, functional groups, and coordination modes of different ligands. Recently, Li et al. synthesized a 3D cross-linked NiCo-MOF via a solvothermal method using 2-amino-5-mercapto-1,3,4-thiadiazole (EAMTD) and BDC as dual ligands. The synergistic coordination of the spatially expansive EAMTD and the linear bidentate BDC effectively prevented excessive structural cross-linking, driving the formation of a highly open porous network. Furthermore, intermolecular π - π stacking established efficient conductive channels, which reduced the charge transfer resistance. The optimized electrode delivered a remarkable specific capacity of 1032 C g^{-1} at 1 A g^{-1} and a high-rate capability of 81% at 5 A g^{-1} [29]. Moreover, ligand competitive coordination effectively introduces structural defects to optimize NiCo-materials. For instance, Lin et al. synthesized defective

NiCo-MOF nanosheets on NF via competitive coordination between monocarboxylic benzoic acid (BA) and dicarboxylic BDC. Substituting bridging BDC linkers with nonbridging BA ligands causes charge repulsion between the MOF layers, which induces swelling and an expanded interlayer spacing, ultimately leading to lattice distortion. This porous and defective structure enlarged the specific surface area ($35.63 \text{ m}^2 \text{ g}^{-1}$) and exposed abundant active sites, accelerating Faradaic reaction kinetics. Consequently, the NiCo-MOF/NF electrode with 10% BA exhibited a capacity of 352.3 mAh g^{-1} at 1 A g^{-1} [30].

2.2. Template Methods for NiCo-Based Materials

Different from the aforementioned approaches, the introduction of external templates can serve as structural guidance to design specific complex morphologies. Through the structure-directing role of template molecules, directional coordination of metal ions with ligands and an orderly self-assembly mechanism can be induced, enabling the controlled construction of specific dimensions and morphologies. Ding et al. constructed a CoNi-ZIF-L superstructure of 3D cross-linked ultrathin porous nanosheets by using polyvinylpyrrolidone (PVP) as a molecular template to induce self-assembly, followed by a subsequent ion-exchange process. During synthesis, selective PVP adsorption drove the anisotropic self-assembly of a sea urchin-like precursor (Co-ZIF-L) (Figure 2h). Subsequently, the Ni^{2+} ion-exchange etching reconstructed the precursor framework into a 3D cross-linked porous architecture. This effectively prevented structural aggregation and maximized the exposure of electroactive sites. Consequently, the optimized $\text{Co}_{6.53}\text{Ni-ZIF-L}$ electrode maintained a capacity retention of 95.3% after 4000 cycles at 5 A g^{-1} (Figure 2i) [31]. Although soft templates effectively control the morphology, the resulting pure MOFs still inherently suffer from poor electrical conductivity. To address these shortcomings, Hao et al. synthesized a NiCo-MOF@MX-NHC composite using NHC-functionalized 2D MXene as a template. The steric hindrance and electron-donating effects of the functional groups regulated the active sites, ensuring uniform MOF nucleation while preventing MXene restacking. This robust hierarchical structure facilitated rapid OH^- transport and exposed abundant redox-active sites. As a result, the optimized electrode delivered an outstanding specific capacitance of 1682.6 F g^{-1} at 1 A g^{-1} and maintained a 68% capacitance retention after 5000 cycles at 20 A g^{-1} [32].

In addition, conductive polymers such as polyaniline (PANI) and poly(para-nitroaniline) (PPNAn) can also serve as effective external templates. On one hand, PANI can act as a connecting template, efficiently encapsulating and bridging the originally loose and irregularly stacked small fragments that make up the NiCo-MOF. This constructs a complete 3D conductive network, overcoming the problems of weak bonding and sluggish reaction kinetics between fragments [33]. On the other hand, PPNAn acts as a high-porosity framework template. Its interwoven fibrous porous network allows the cauliflower-shaped or planar granular NiCo-MOFs to be completely embedded within it, forming a uniform composite with mesoporous characteristics, which significantly expands the electrode-electrolyte contact area [34]. Beyond the aforementioned conductive polymer networks, classical hard and soft templates are extensively utilized for the precise morphological engineering of NiCo-based materials. For instance, ZIFs, SiO_2 nanospheres, surfactants (e.g., CTAB), and self-sacrificial precursors (e.g., SiO_2 @RF resin microspheres) are commonly employed to construct unique microstructures, such as 1D nanorods, hierarchical hollow microspheres, and porous hollow nanocages. These template-directed hollow and porous architectures not only provide massive internal voids to effectively buffer volume expansion of NiCo-based materials during rapid charge-discharge processes but also drastically shorten the diffusion pathways for electrolyte ions. Ultimately, the introduction of these templating strategies significantly enhances both the rate kinetics and ultra-long cycling stability of NiCo-based SCs [35–39].

Although morphology engineering has been widely demonstrated to enhance the electrochemical performance of NiCo-based materials by increasing surface area, exposing active sites, and facilitating ion/electron transport, its role should be understood as a structural optimization rather than a fundamental modification of the material's intrinsic properties. In most cases, improvements derived from morphology control remain constrained by the underlying electronic structure of the active phase, and therefore cannot fully resolve limitations in conductivity or long-term stability. Moreover, different morphology control strategies involve distinct trade-offs. Simple parameter regulation is relatively straightforward but often lacks precise structural control and reproducibility, whereas ligand-assisted and template-assisted approaches enable more complex architectures at the cost of increased synthetic complexity and reduced scalability. As a result, morphology engineering should be considered an enabling strategy that is most effective when combined with compositional tuning or interfacial engineering, rather than a standalone solution for performance enhancement.

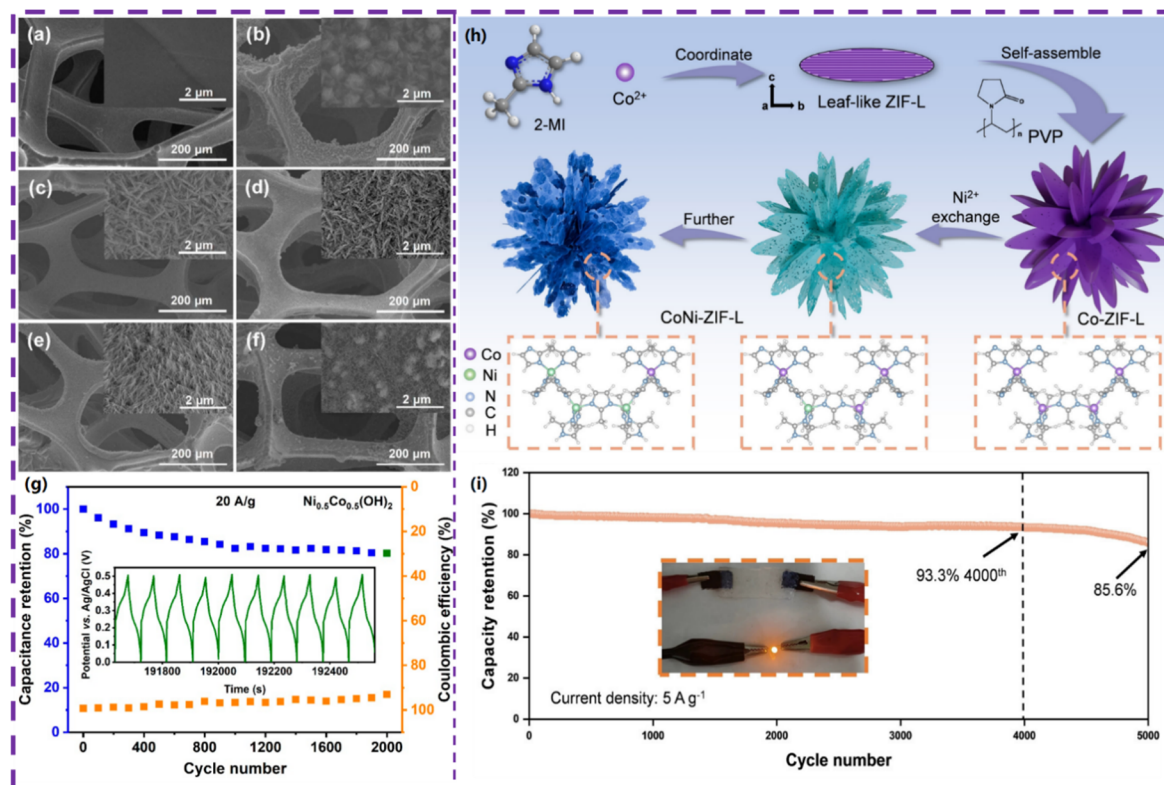


Figure 2. Scanning electron microscope (SEM) images of the samples at different Ni:Co ratios: (a) bare nickel foam; (b) 9:1; (c) 7:3; (d) 5:5; (e) 3:7; (f) 1:9. (g) Cycling performance and coulombic efficiency of the $\text{Ni}_{0.5}\text{Co}_{0.5}(\text{OH})_2$ electrode. Adapted from [16] under the terms of the Creative Commons Attribution (CC BY 4.0) license. (h) Schematic of the synthetic route for CoNi-ZIF-L. (i) Long-term cycling stability of the assembled asymmetric flexible SC at 5 A g⁻¹ over 5000 cycles (inset demonstrates an LED powered by the device). Reproduced with permission [31]. Copyright 2024, Wiley-VCH.

3. Self-Supporting Substrates for NiCo-Based Materials in SCs

Although microscopic morphology engineering optimizes NiCo-based materials, conventional unsupported electrodes still suffer from sluggish electron transport and structural degradation due to the lack of macroscopic conductive frameworks. Self-supporting architectures address this by growing active NiCo-based materials directly *in situ* onto conductive substrates. This binder-free approach maximizes the proportion of electroactive species and boosts energy density. Furthermore, the seamless integration minimizes interfacial resistance for rapid electron transfer, while the robust anchoring buffers structural strain, ensuring superior long-term cyclic stability. Currently, these substrates for loading NiCo-based materials are primarily categorized into metal-based and carbon-based substrates.

3.1. Metal-Based Substrates for Supporting NiCo-Based Materials in SCs

Metal-based self-supporting substrates are the most widely used carriers for NiCo-based electrodes, owing to their intrinsic high metallic conductivity, 3D interconnected structure, and excellent mechanical strength. Among them, the NF substrate has abundant loading sites for active materials, and its high intrinsic conductivity significantly reduces the interfacial impedance of the electrode. Meanwhile, the in-situ growth strategy enables tight bonding between the NiCo-based materials and NF, avoiding side reactions and shedding issues caused by binders. As a prototypical demonstration of macroscopic support, Zhou et al. synthesized hierarchical-porous $\text{Co}(\text{OH})_2/\text{Ni}(\text{OH})_2$ micro-rod arrays on NF via solvothermal synthesis and self-sacrificial ion exchange. This binder-free 3D framework effectively circumvents the severe agglomeration typically associated with traditional powder electrodes, minimizes interfacial resistance, and buffers mechanical strain during OH^- reaction. Consequently, the electrode delivered a high areal capacitance of 16.3 F cm⁻² at 2 mA cm⁻² and maintained a 73.5% retention after 10,000 cycles at 80 mA cm⁻² [40]. Building upon these fundamental advantages, NF substrates can also accommodate high active-material loadings. Building on this advantage, Lu et al. fabricated hierarchically hollow $\text{Ni}(\text{OH})_2/\text{Co}(\text{OH})_2$ micropillars on NF via ligand regulation and in-situ ion-exchange processes (Figure 3a). The interconnected 3D macroporous NF network provides a strong anchoring platform,

sustaining an ultrahigh active mass loading of 23.3 mg cm^{-2} without detachment. During the charging process, electrons rapidly pass through the 3D hollow structure, which facilitates the efficient accumulation/retention of a large number of OH^- (Figure 3b,c). This intimate conductive interface facilitates rapid electron transfer and alleviates volume expansion, yielding an outstanding 53.6 F cm^{-2} at 1 mA cm^{-2} [41]. This result also highlights the importance of evaluating NiCo-based electrodes at practically relevant mass loadings, since high gravimetric performance obtained at low loading does not necessarily translate into comparable areal or volumetric performance in practical electrodes. Furthermore, the 3D macroscopic skeleton of NF can also function as a superior orientation platform to direct the ordered growth of functional microstructures. For instance, Liu et al. employed bimetallic nickel/cobalt ions and a thiophene ligand (2,5-thiophenedicarboxylic acid) to construct a regular array of 2D NiCo-MOF nanosheets on NF via a facile one-step hydrothermal approach. The modified NF substrate guides the vertical alignment of 2D nanosheets, effectively preventing the restacking and dead-zone agglomeration of the active materials. Concurrently, this direct integration creates highly efficient pathways for electron/ OH^- transport, enabling the optimized NiCo-MOF/NF-3-2 electrode to deliver a high specific capacity of 615.7 C g^{-1} at 1 A g^{-1} , along with a high capacitance retention of 80.3% after 5000 cycles at 10 A g^{-1} [42].

Researchers have explored copper foam (CF) as an alternative macroscopic scaffold. Its three-dimensional porous structure can accommodate volume changes of NiCo-based materials, while its metallic framework provides conductive pathways for electron transport. For example, Bi et al. utilized CF as both a conductive substrate and an in-situ copper source to construct hierarchical CuO@NiCo-LDH heterostructures (Figure 3d). In this unique architecture, nanoflake-assembled NiCo-LDH hollow nanocages are strung onto CuO nanorods derived from the surface etching and oxidation of the CF. Based on this design, the CF-derived CuO nanorod arrays function as a robust 3D skeleton to prevent the agglomeration of the NiCo-LDH hollow nanocages and minimize interfacial resistance. Consequently, the electrode delivered a large areal capacitance of 5607 mF cm^{-2} at 1 mA cm^{-2} and maintained a 93.1% capacitance retention after 5000 cycles (Figure 3e). Moreover, the assembled ASC achieved a maximum energy density of 47.3 Wh kg^{-1} at 800 W kg^{-1} and showed only a 6.8% capacitance decline rate after 10,000 cycles [43]. Building upon this dual-functional advantage, CF also supports more complex multi-metallic networks. Lei et al. employed CF to design a binder-free core-shell nanoflower-like CuO/CF@NiCoMn-OH electrode via an MOF-assisted strategy. Here, CF provides the essential Cu source for bunch-like CuO nanowires, which anchor uniform ZIF-67 dodecahedrons. This 3D integration ensures fast OH^- diffusion and shortens electron routes, yielding a low internal resistance. Consequently, the electrode achieved an outstanding areal capacitance of 26.8 F cm^{-2} at 8 mA cm^{-2} . Furthermore, the assembled hybrid supercapacitor (HSC) delivered a notable energy density of 37.28 Wh kg^{-1} at a power density of 170 W kg^{-1} , highlighting the great potential of CF for high-loading SCs [44].

While CF provides excellent conductivity, its vulnerability to alkaline corrosion during prolonged cycling remains a critical challenge. Consequently, mechanically stable, cost-effective, and reusable flexible stainless steel (FSS) substrates have been adopted as a reliable alternative to guarantee long-term structural integrity. Gurav et al. utilized a cost-effective FSS substrate to synthesize NiCo-MOFs (NCMS) via a post-synthesis etching and ion-exchange approach. The FSS acts as an affordable and reusable current collector to provide essential mechanical stability for the direct growth of a porous, interconnected sheet-like architecture. Consequently, by optimizing the nickel precursor concentration, the resulting electrode delivered an outstanding specific capacity of 206 mAh g^{-1} at 5 mV s^{-1} . Furthermore, the assembled symmetric aqueous device maintained 69% capacitance retention over 3000 cycles at 15 A g^{-1} [45]. To further explore the economic advantages of FSS, Gurav et al. designed core-shell NiCo-MOFs via a cost-efficient post-synthesis method. Here, FSS acts as an affordable macroscopic collector supporting a highly open 3D architecture. Benefiting from extensive active-site exposure and low resistance, the electrode delivered an impressive capacitance of 1016 F g^{-1} at 2 A g^{-1} , with the solid-state device achieving an energy density of 8.19 Wh kg^{-1} [46].

3.2. Carbon-Based Substrates for Supporting NiCo-Based Materials in SCs

While metallic substrates offer excellent initial conductivity, they are highly susceptible to mechanical fatigue under continuous deformation during long-term cycling. Dynamic mechanical stress during routine wear inevitably induces microcrack propagation and structural fracture in metals, severely compromising the lifespan of flexible devices [47]. Consequently, researchers have shifted their focus toward carbon-based substrates (e.g., carbon cloth (CC), carbon cloth textiles (CCT) and multidimensional carbon materials) due to their combined advantages of flexibility, high conductivity, and favorable fatigue resistance, making them suitable substrates for flexible and wearable SCs.

CC is the most common carbon material for self-supporting substrates in SCs. Surface modification of CC is a critical step to introduce abundant functional groups for the growth of NiCo materials and provide contact sites that enhance interfacial bonding. For instance, Zhang et al. pre-treated the CC with H_2O_2 solution to introduce abundant oxygen-containing functional groups (such as $-\text{OH}$ and $-\text{C}=\text{O}$), converting its surface from hydrophobic to hydrophilic. This effectively regulated the preferential growth of $\text{CoNi}_{0.5}$ -MOF along the (031) crystal plane, yielding a cross-linked structure of nanosheets and nanorods. Such a hybrid architecture provides effective buffer space for volume expansion during the charging and discharging process (achieving an 88% capacitance retention after 6000 cycles at 10 A g^{-1}). Moreover, the in-situ chemical bonding eliminates the need for binders, significantly reducing the charge transfer impedance to 0.38Ω [48]. Similarly, Liang et al. employed a binder-free strategy to construct hollow CoNiOOH nanorods on activated carbon cloth (ACC). This method initially grew $\text{Ni}(\text{OH})_2$ nanosheets on the ACC as anchoring precursors, followed by the deposition of CoNi -MOF and subsequent in-situ conversion into a porous hollow structure via electrochemical induction. This highly open heterogeneous network significantly facilitates the rapid diffusion of electron/ OH^- . Consequently, the self-supported electrode achieved a high areal specific capacitance of 11.6 F cm^{-2} at 2 mA cm^{-2} . Furthermore, the assembled ASC exhibited a high areal energy density of $0.732 \text{ mWh cm}^{-2}$ and maintained an outstanding capacitance retention of 98.59% after 10,000 cycles [49]. Beyond conventional CC, the intrinsic flexibility of CCT makes it a suitable current collector for flexible all-solid-state supercapacitors. Nanda et al. fabricated a flexible electrode by directly integrating bimetallic NiCo-MOF onto CCT via in-situ hydrothermal growth. This design leverages the block-like morphology of the NiCo-MOF and its unique strain-driven Moiré patterns to provide abundant active sites and rapid OH^- pathways, while the mechanical robustness of the CCT accommodates physical deformations during service. The electrode delivered a high specific capacitance of 778.2 F g^{-1} at 1 A g^{-1} . The all-solid-state ASC achieved a notable energy density of 41.6 Wh kg^{-1} and retained 79.65% of its capacitance after 10,000 cycles at 15 A g^{-1} , highlighting its potential in SCs for wearables [50].

To further push the limits of specific surface area and microstructural manipulation, researchers have progressively expanded carbon materials self-supporting substrates beyond CC to multi-dimensional advanced carbon materials (e.g., 1D carbon nanotubes (CNTs), 2D graphene, and 3D porous biomass-derived carbon). Niu et al. utilized NiCo-MOF as an outstanding sacrificial template to in-situ construct 2D porous microarrays interwoven with NiCo-LDH and carbon nanosheets on a CNT network. This highly interconnected 1D tubular skeleton effectively prevents microarray stacking and broadens ion diffusion channels, enabling the assembled ASC to deliver a high energy density of 37.4 Wh kg^{-1} at a power density of 750 W kg^{-1} , while maintaining a 94.5% capacitance retention after 5000 cycles [51]. Similarly, Zheng et al. employed a CNT film as a current collector to grow a multi-component collaborative structure featuring NiCoP-modified Cu-MOF. This strategy not only exploits the high-speed electron channels provided by CNTs but also stimulates deep electrochemical activity through the introduction of NiCoP, endowing the self-supporting electrode with a remarkable capacitance of 1154 F g^{-1} at 1 A g^{-1} . The assembled device achieved an energy density of 58.2 Wh kg^{-1} at 800 W kg^{-1} and retained 80.6% capacitance after 10,000 cycles at high current density [52].

2D graphene can serve as an effective conductive support for NiCo-based materials owing to its high specific surface area and favorable electron-transport characteristics. He et al. converted MOFs into low-crystallinity NiCo-LDH nanosheets on vertical graphene (VG) arrays via a sol-gel method (Figure 3f). In this NiCo-LDH/VG system, density functional theory (DFT) calculations suggested that the Mott-Schottky heterostructure formed between LDH and VG induced a built-in electric field, thereby facilitating interfacial electron transfer. The resulting heterostructure electrode delivered an areal capacitance of $5513.8 \text{ mF cm}^{-2}$ at 0.5 mA cm^{-2} , demonstrating outstanding energy-storage performance (Figure 3g). Furthermore, the fabricated hybrid device exhibited a notable energy density of $0.4048 \text{ mWh cm}^{-2}$ at 1.6 mW cm^{-2} with a 92.0% capacitance retention over 10,000 cycles at 40 mA cm^{-2} [53]. Similarly, pursuing an effective and low-consumption fabrication process, Yang et al. utilized rapidly reduced graphene oxide nanosheets (rGNS) at room temperature as nucleation substrates to induce the uniform growth of granular NiCo-LDH. This tight 2D interfacial bonding enables the material to deliver an outstanding capacitance of 2179 F g^{-1} at 1 A g^{-1} and exhibit a robust capacitance retention of 88% after 3000 cycles at 1 A g^{-1} [54].

With the rise of green and sustainable energy storage concepts, biomass-derived carbon with natural 3D hierarchical pores (e.g., carbonized wood, CW) has stood out, providing favorable biomimetic mass transport channels for thick electrodes and high active-material mass loadings. Zhang et al. proposed a macro-micro dual-control strategy by *in situ* growing bimetallic NiCo-MOFs on carbonized wood (CW). Macroscopically, the straight CW microchannels act as a robust, binder-free conductive skeleton for fast electrolyte penetration. Microscopically, Co^{2+} doping effectively expands the unit cell volume for ultrafast ion transport. Consequently, the NiCo-MOF@CW electrode achieved a high areal capacitance of 4960 mF cm^{-2} at 0.6 mA cm^{-2} . The assembled asymmetric device delivered an energy density of 1.88 mWh cm^{-2} at 2.88 mW cm^{-2} with an 83.6% retention over

2000 cycles at 10 mA cm^{-2} [55]. Also based on the biomimetic space design of wood-derived carbon, Xiong et al. introduced a surface engineering strategy involving pyrolysis and moderate acid etching to convert pre-grown NiCo-MOF into a Ni/NiO/CoO-CW composite. This specific acid-etching treatment effectively eliminates disordered metals and metal oxides, resulting in an interconnected 3D hollow carbon structure with an optimized chemical surface. This modification effectively addresses the common issues of low energy density and poor structural stability in wood carbon composites. Consequently, the assembled symmetric SC delivered an energy output of 0.67 mWh cm^{-2} at 2.5 mW cm^{-2} and sustained a 96.21% retention over 10,000 long-term cycles [56]. As shown below, Table 1 summarizes the reported carbon-based substrates in NiCo-MOF and their corresponding electrochemical properties.

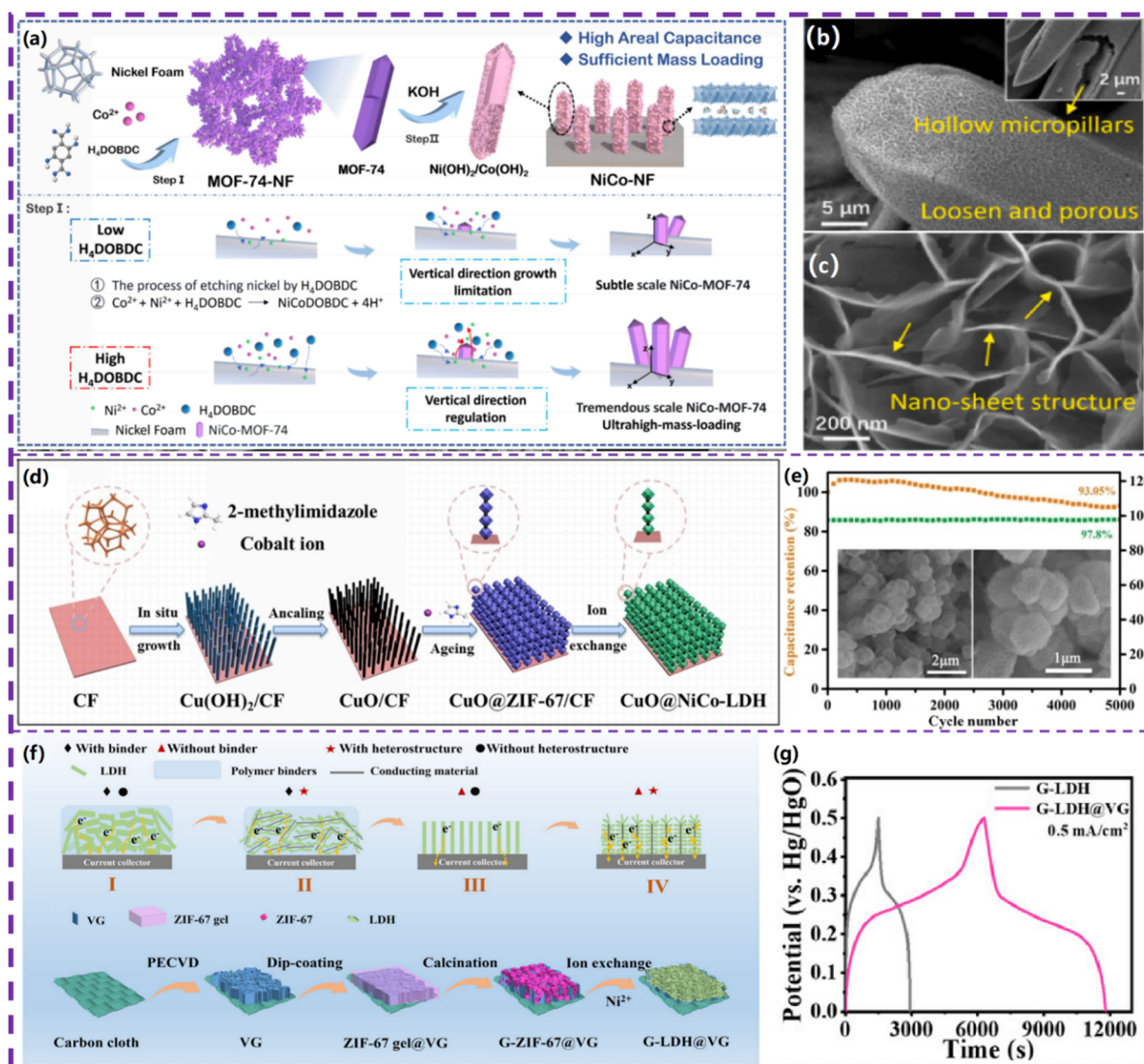


Figure 3. (a) Schematic illustration of the synthesis procedure for the hollow micropillar NiCo-NF composites, (b) SEM image detailing the hollow structure, and (c) HR-TEM images of the M-NiCo-NF composites. Reproduced with permission [41]. Copyright 2025, Elsevier. (d) Schematic showing the construction of CuO@NiCo-LDH/CF. (e) Cycling stability and coulombic efficiency of the CuO@NiCo-LDH/CF during 5000 cycles (inset shows the SEM images of CuO@NiCo-LDH/CF before and after cycling). Reproduced with permission [43]. Copyright 2022, Wiley-VCH. (f) Schematics of nanoscale electron mobility across various LDH configurations (I–IV), and the preparation route for the G-LDH@VG Mott-Schottky heterostructure. (g) GCD curves at 0.5 mA cm^{-2} . Reproduced with permission [53]. Copyright 2024, Wiley-VCH.

In summary, metal-based substrates represent mature and extensively utilized self-supporting platforms in SCs. Specifically, NF serves as the most adopted substrate for NiCo-MOF electrodes, CF breaks through rate-performance limits via integrated conductive-active designs, and FSS satisfies the demands for robust mechanical stability and cost-effectiveness. Meanwhile, carbon-based current collectors steer the future toward diversified development, where CC delivers exceptional flexibility, low-dimensional nanocarbons optimize electron/ion

kinetics, and biomass carbon offers a sustainable, highly porous biomimetic avenue. Beyond initial architecture, the in-situ derivatization method further enhances conductivity and cycling stability, significantly broadening the practical application of self-supporting NiCo-based electrodes for next-generation SCs.

Table 1. NiCo-based materials with carbon substrates and their corresponding electrochemical performance.

Substrates	Samples	Electrode Performance	Device Type	Energy Density	Power Density	Cyclic Stability	Refs.
CC	CoNi _{0.5} -MOF	1337.5 F g ⁻¹ (1 A g ⁻¹)	ASC	61.46 Wh kg ⁻¹	1244.56 W kg ⁻¹	88% (6000 cycles)	[48]
CC	CoNiOOH	11.6 F cm ⁻² (2 mA cm ⁻²)	ASC	0.732 mWh cm ⁻²	1.6 mW cm ⁻²	98.59% (10,000 cycles)	[49]
CC	Ni/Co-MOF	778.2 F g ⁻¹ (1 A g ⁻¹)	ASC	41.6 Wh kg ⁻¹	1062 W kg ⁻¹	79.65% (10,000 cycles)	[50]
CC	NiCo-BTC	644.4 C g ⁻¹ (0.5 A g ⁻¹)	Flexible ASC	32.4 Wh kg ⁻¹	346 W kg ⁻¹	91.2% (8000 cycles)	[57]
CC	CoNi-MOF	43.58 F cm ⁻² (5 mA cm ⁻²)	ASC	1.25 mWh cm ⁻²	4 mW cm ⁻²	98.9% (10,000 cycles)	[58]
CC	NiCo-MOF	1.1805 C cm ⁻² (3 mA cm ⁻²)	-	-	-	97.6% (5000 cycles)	[59]
CNTs	CNT@NiCo-LDH	1159.2 F g ⁻¹ (1 A g ⁻¹)	ASC	37.4 Wh kg ⁻¹	750 W kg ⁻¹	94.5% (5000 cycles)	[51]
CNTs	NiCoP/HKUST-1@CNTs	1154 F g ⁻¹ (1 A g ⁻¹)	ASC	58.2 Wh kg ⁻¹	800 W kg ⁻¹	80.6% (10,000 cycles)	[52]
MWCNTs	NiCo-MOF	1010 F g ⁻¹ (0.5 A g ⁻¹)	ASC	19.7 Wh kg ⁻¹	250 W kg ⁻¹	98% (3000 cycles)	[60]
rGNS	NiCo-LDH/rGNS	2179 F g ⁻¹ (1 A g ⁻¹)	-	-	-	88% (3000 cycles)	[54]
EGP	NCMOF	2.41 F cm ⁻² (0.5 mA cm ⁻²)	ASC	0.11 mWh cm ⁻²	0.75 mW cm ⁻²	71.2% (10,000 cycles)	[61]
VG	NiCo-LDH/VG	5.5138 F cm ⁻² (0.5 mA cm ⁻²)	HSC	0.4048 mWh cm ⁻²	1.6 mW cm ⁻²	92.0% (10,000 cycles)	[53]
VGN	NiCo MOF	950 F g ⁻¹ (1 A g ⁻¹)	solid-state ASC	36.5 Wh kg ⁻¹	7000 W kg ⁻¹	88.5% (10,000 cycles)	[62]
CW	NiCo-MOF@CW	4.960 F cm ⁻² (0.6 mA cm ⁻²)	ASC	1.88 mWh cm ⁻²	2.88 mW cm ⁻²	83.6% (2000 cycles)	[55]
CW	Ni/NiO/Co-CW-4	16.76 F cm ⁻² (5 mA cm ⁻²)	solid-state ASC	0.67 mWh cm ⁻²	2.5 mW cm ⁻²	96.21% (10,000 cycles)	[56]
CW	CoNiP-C	2.630 F cm ⁻² (5 mA cm ⁻²)	ASC	0.0360 mWh cm ⁻²	0.3375 mW cm ⁻²	87.5% (5000 cycles)	[63]
CW	NiCo ₂ O ₄	1730 F g ⁻¹ (1 A g ⁻¹)	ASC	56.1 Wh kg ⁻¹	349 W kg ⁻¹	75.2% (10,000 cycles)	[64]

Abbreviations: EGP, partially-exfoliated graphite paper; VGN, vertical graphene nanosheets; VG, vertical graphene; CW, carbonized wood; CC, carbon cloth; CNTs, carbon nanotubes; MWCNTs, multiwalled carbon nanotubes; ASC, asymmetric supercapacitor; HSC, hybrid supercapacitor. Note: For clarity, the electrochemical metrics in Table 1 are normalized to consistent units within the same dimensional basis, while gravimetric and areal metrics are retained separately because direct conversion requires additional parameters such as active-material loading and operating voltage window.

4. MOF-Derived NiCo Materials for SCs

Although self-supporting architectures minimize interfacial contact resistance, they cannot alter the intrinsic properties of active materials. Whether fabricated as traditional powders or integrated into self-supporting substrates, NiCo-based materials still suffer from poor electrical conductivity due to insulating organic ligands, alongside structural fragility during prolonged Faradaic cycling. To overcome these bottlenecks, derivatization has emerged as an essential strategy. Converting NiCo-MOF precursors into inorganic derivatives (e.g., oxides, sulfides, or LDHs) can improve electrical transport and structural robustness by transforming the organic-linker framework. Depending on the derivative composition and conversion conditions, the hierarchical porous features of the precursor may be retained to varying degrees.

4.1. MOF-Derived Metal Oxides and Hydroxides Materials for SCs

Among the diverse derivatization strategies, converting NiCo-MOF precursors into metal oxides or LDHs represents the most direct and widely adopted approach. Through precisely controlled thermal annealing in an air atmosphere or chemical etching, the organic ligands are gently decomposed or substituted, while the structural hierarchy of the parent MOF is well-preserved. MOF-derived NiCo oxides typically possess superior chemical stability and enriched oxygen vacancies, which serve as highly active shallow donor states to further accelerate electron conduction. Concurrently, MOF-derived NiCo-LDHs inherit the classic layered structure, offering expansive interlayer spacing for rapid ion intercalation/deintercalation [65,66]. Converting MOF precursors into

metal oxide derivatives is an effective strategy to overcome intrinsic kinetic limitations. Lu et al. employed NiCo-MOFs as precursors to derive a series of layered NiO@NiCo₂O₄ composites through air calcination at various temperatures for 2 h. After the calcination process, the precursors smoothly transformed into interconnected micro-sheet networks. This structural evolution not only maximized the exposure of electroactive surfaces but also endowed the material with a solid skeleton. Consequently, the electrode calcined at 400 °C maintained a capacity retention of 78.73% after 4,500 cycles at 15 A g⁻¹, significantly extending the cycle life of NiCo-based materials in SC applications [67]. Furthermore, Chettiannan et al. first utilized sodium dodecyl sulfate to direct the assembly of 2D MOF nanosheets into flower-like precursors. Subsequently, the organic frameworks were thoroughly decomposed during air calcination at 600 °C for 4 h, yielding a highly porous flower-like NiO/Co₃O₄ architecture. This structure not only provided abundant redox sites but also optimized reaction kinetics through the tight contact between different metal oxide nanoparticles. Consequently, the electrode achieved a high specific capacity of 1971.4 F g⁻¹ at 1 A g⁻¹ and maintained a capacity retention of 92.85% after 5000 GCD cycles [68]. Furthermore, extensive research has demonstrated that calcined NiCo-MOF-derived metal oxide electrodes can effectively overcome the intrinsic defects of severe agglomeration and sluggish kinetics of traditional materials through rational morphology engineering (such as constructing ultrathin nanosheets or highly porous structures), thereby significantly boosting the electrochemical reactivity, specific capacitance, and structural stability of SCs [69–72].

Similarly, NiCo-hydroxide derivatives provide an alternative method for reconstructing highly reactive electrochemical interfaces within the NiCo materials. Cao et al. synthesized spherical NiCo-MOF powders via a solvothermal method and subsequently transformed them into 2D NiCo-LDH@Ni(OH)₂ heterogeneous nanosheets through an alkaline oxidation treatment using an aqueous solution of NaOH and (NH₄)₂S₂O₈. Benefiting from the unique 2D nanostructure and the synergistic effects within the multicomponent heterojunction, the electrochemical reactivity was significantly enhanced. Consequently, this composite electrode delivered a high specific capacity of 754.8 C g⁻¹ at 1 A g⁻¹, and the assembled HSC maintained an 89.0% capacity retention over 5000 cycles with an energy output of 30.6 Wh kg⁻¹ [73]. Beyond 2D designs, constructing 3D hollow architectures offers another powerful strategy to prevent the severe restacking of NiCo-LDH nanosheets and accelerate ion diffusion. Zhao et al. utilized polyhedral ZIF-67 as self-sacrificial templates. Driven by the synergistic Kirkendall effect and Ostwald ripening during a solvothermal process, hollow NiCo-LDH nanocages were assembled by quasi-vertical nanosheet arrays, which provide a high specific surface area (288.2 m² g⁻¹) for rapid OH⁻ transport and buffer volume expansion during continuous Faradaic redox reactions. Consequently, the optimal electrode delivered 2203.6 F g⁻¹ at 2 A g⁻¹, and the assembled HSC achieved a superior energy density of 57.3 Wh kg⁻¹ at 1600 W kg⁻¹ with 73.1% capacitance retention after 2000 cycles [74].

In short, both MOF-derived NiCo-based oxides and hydroxides have demonstrated tremendous success in breaking structural and kinetic bottlenecks; However, the pursuit of more favorable electronic structures and faster charge-transfer kinetics has stimulated increasing interest in other derivatives, particularly sulfides and phosphides.

4.2. MOF-Derived Ni/Co Sulfides Electrode Materials for SCs

Compared with many oxide and hydroxide counterparts, transition-metal sulfides generally exhibit higher electrical conductivity and rich redox activity, which can facilitate charge-transfer kinetics and pseudocapacitive reactions. Substituting oxygen with sulfur can narrow the electronic bandgap of the material. The sulfidation process involves a controlled chemical reaction between sulfur sources (e.g., thiourea, Na₂S, thioacetamide (TAA)) and metal centers (Ni²⁺, Co²⁺) within the MOF framework. This process transforms the parent MOF into highly active Ni-Co-S-based composites (e.g., NiCo₂S₄, Ni₃S₂/Co₃S₄), successfully reconstructing the structure and optimizing the electronic environment. Consequently, this approach overcomes the bottlenecks of sluggish kinetics and insufficient active-site utilization in pristine NiCo-MOFs, thereby significantly boosting the electrochemical performance of the composites in SCs.

Gas-phase sulfidation is an effective method that combines thermally driven solid-state reactions with gas-phase deposition. By intimately mixing the NiCo-MOF precursor with a solid sulfur source (such as sulfur powder or thiourea) and heating under an inert atmosphere, the precursors are effectively converted into high-performance NiCo-sulfides. During this process, organic ligands are carbonized to form a conductive network, while the decomposing sulfur sources release active (S_x, H₂S), which react with exposed Ni/Co metal ions. For instance, Tian et al. utilized bimetallic NiCo-BTC organic frameworks as templates and sulfur powder as the sulfur source to prepare a sulfur vacancy-rich NiCo₂S₄/C fiber through a one-step in-situ carbonization-vulcanization method. Within this 3D nanoflower structure, the abundant sulfur vacancies exposed more redox active sites, while the expandable carbon conductive network accelerated electron transport. Consequently, this optimized electrode exhibited an impressive capacitance of 1934 F g⁻¹ at 1 A g⁻¹, coupled with a high capacity retention of 93.2% after

5000 cycles at 5 A g⁻¹ [75]. To further optimize the template design, Zheng and Wang adopted sublimed sulfur, mixing the NiCo-LDH@CoBTC precursor with sulfur powder at an optimal mass ratio of 1:2.5. The porous wrinkled microspherical Co_xNi_{1-x}S₂ structures were obtained after calcination at 450 °C for 2 h under an Ar atmosphere. Under these conditions, the precursor was completely converted into bimetallic sulfides while retaining the porous structural features of the original CoBTC MOF template. Benefiting from the synergistic effect between Ni and Co, this porous architecture effectively promoted the OH⁻ and electrons migration, enabling the sulfide matrix to provide a capacitance of 1243.69 F g⁻¹ at 1 A g⁻¹ [76]. Exploring sustainable material sources, Hu et al. innovatively recovered cobalt ion leachate from spent lithium cobalt oxide batteries to synthesize spherical Co_xNi_{3-x}-S-MOF precursors. By implementing a controlled carbonization and sulfidation process using thiourea in an Ar atmosphere, a spherical core-shell structured Co_xNi_{3-x}-S bimetallic sulfide was derived. This MOF-to-sulfide derivation strategy created a durable structure with a significantly increased specific surface area. Remarkably, the assembled ASC device highlighted its practical viability by achieving a remarkable energy density of 38.6 Wh kg⁻¹ at 800 W kg⁻¹ [77].

On the other hand, liquid-phase sulfidation typically involves the use of soluble sulfur sources (such as Na₂S or TAA) in a hydrothermal or solvothermal environment, enabling precise morphological etching, ion exchange, and in-situ array growth. For example, Jin et al. utilized NiCo-MOF spheres and TAA to construct amorphous NiCo₂S₄ hollow structures via Ostwald ripening and ion exchange-etching strategies. This unique amorphous hollow structure not only provided internal voids to enhance redox active sites and facilitate ion diffusion, but also improved intrinsic conductivity and mitigated volume expansion during electrochemical processes. Thus, the optimized electrode demonstrated a good specific capacitance of 1019 F g⁻¹ at 1 A g⁻¹ [78]. To meet the demand for flexible and wearable devices, Zhao et al. grew Co-MOF solid nanoarrays on electrochemically ACC. Hollow and ultrathin Ni-Co-S nanosheet arrays on ACC were fabricated through a unique hydrolysis and etching process in the presence of Ni(NO₃)₂ and Na₂S. These ultrathin nanosheets effectively shortened the OH⁻ diffusion pathway and enriched the redox active sites. Ultimately, the flexible electrode delivered a remarkable specific capacitance of 2392 F g⁻¹ at 1 A g⁻¹. More importantly, the corresponding HSC delivered an energy density of 30.1 Wh kg⁻¹ at 800.2 W kg⁻¹ and retained 82% of its capacitance after 10,000 cycles [79]. To further enrich the morphological diversity of binder-free electrodes, Xiong et al. employed a ZIF-assisted hydrothermal method followed by TAA sulfidation to construct 3D-networked NiCo₂S₄ nanosphere arrays directly on NF. This synergistic architecture coupled the highly conductive NF scaffold with a porous 3D network, facilitating rapid electron transfer and electrolyte penetration. Consequently, the electrode delivered a specific capacitance of 1286.6 C g⁻¹ at 1 A g⁻¹, enabling the assembled ASC to achieve a superior specific energy of 74.0 Wh kg⁻¹ at 850.0 W kg⁻¹ [80].

Building upon both liquid-phase and gas-phase sulfidation strategies, numerous MOF-derived NiCo sulfide electrodes have been investigated for SCs, and their corresponding electrochemical performance is summarized in Table 2. Liquid-phase sulfidation typically involves reacting the MOF precursor with dissolved sulfur sources (e.g., Na₂S, TAA) under solvothermal or hydrothermal conditions. This method benefits from relatively mild reaction conditions and allows for precise morphological control; however, it may face challenges related to solvent residues and by-product formation. On the other hand, gas-phase sulfidation utilizes vaporized solid sulfur or gaseous sulfur sources (such as H₂S) during thermal treatment under an inert atmosphere. This approach effectively avoids liquid-phase impurities and excels at preserving the original MOF framework, yet it often demands stringent equipment specifications and precise temperature control. Overall, both liquid- and gas-phase sulfidation can improve the electrical conductivity and electrochemical activity of NiCo-based materials. However, the extent of structural preservation and cycling stability strongly depends on the sulfide composition, morphology, conversion conditions, and electrode architecture.

Table 2. The sulfide derivatives of NiCo-MOF electrodes and the corresponding electrochemical properties in SCs.

Sulfidation Methods	Samples	Electrode Performance	Device Type	Energy Density	Power Density	Cyclic Stability	Refs.
Gas-phase sulfidation	Co _x Ni _{1-x} S ₂	1243.69 F g ⁻¹ (1 A g ⁻¹)	ASC	38.19 Wh kg ⁻¹	800 W kg ⁻¹	90% (1000 cycles)	[76]
Gas-phase sulfidation	Co _x Ni _{3-x} -S	1285 F g ⁻¹ (1 A g ⁻¹)	ASC	38.6 Wh kg ⁻¹	800 W kg ⁻¹	71% (3000 cycles)	[77]
Gas-phase sulfidation	NiCo ₂ S ₄ /C	1934 F g ⁻¹ (1 A g ⁻¹)	HSC	50.24 Wh kg ⁻¹	800 W kg ⁻¹	93.2% (5000 cycles)	[75]
Gas-phase sulfidation	NiCoS/d-Ti ₃ C ₂	758.9 C g ⁻¹ (1 A g ⁻¹)	HSC	22.6 Wh kg ⁻¹	400 W kg ⁻¹	91.2% (10,000 cycles)	[81]
Gas-phase sulfidation	(Co _x Ni _{1-x}) ₂ P/	1567 F g ⁻¹				89.7%	
sulfidation	Co _x Ni _{1-x} -S	(1 A g ⁻¹)		-	-	(5000 cycles)	[82]

Table 2. Cont.

Sulfidation Methods	Samples	Electrode Performance	Device Type	Energy Density	Power Density	Cyclic Stability	Refs.
Gas-phase sulfidation	NiCo ₂ O ₄ @NiCo ₂ S ₄	1872 F g ⁻¹ (1 A g ⁻¹)	HSC	35.6 Wh kg ⁻¹	1500 W kg ⁻¹	78% (2000 cycles)	[83]
Gas-phase sulfidation	mNi _{0.32} Co _{0.68} S ₂	1698 F g ⁻¹ (2 A g ⁻¹)	ASC	37 Wh kg ⁻¹	800 W kg ⁻¹	66% (1000 cycles)	[84]
Liquid-phase sulfidation	NiCo ₂ S ₄	1019 F g ⁻¹ (1 A g ⁻¹)	ASC	31.33 Wh kg ⁻¹	851.2 W kg ⁻¹	77.1% (6000 cycles)	[78]
Liquid-phase sulfidation	NiCo ₂ S ₄ /ACC	2392 F g ⁻¹ (1 A g ⁻¹)	HSC	30.1 Wh kg ⁻¹	800.2 W kg ⁻¹	82% (10,000 cycles)	[79]
Liquid-phase sulfidation	Ni-Co-S@NF	1286.6 C g ⁻¹ (1 A g ⁻¹)	ASC	74.0 Wh kg ⁻¹	850.0 W kg ⁻¹	70% (5000 cycles)	[80]
Liquid-phase sulfidation	CoS _{1.097} /Ni ₉ S ₈	596.4 C g ⁻¹ (2 A g ⁻¹)	ASC	37.2 Wh kg ⁻¹	375.9 W kg ⁻¹	99.3% (10,000 cycles)	[85]
Liquid-phase sulfidation	CoNi ₂ S ₄	5.24 F cm ⁻² (3 mA cm ⁻²)	HSC	59.41 Wh kg ⁻¹	999.98 W kg ⁻¹	89.24% (10,000 cycles)	[86]
Liquid-phase sulfidation	CNTs/Ni-Co-S	734 C g ⁻¹ (1 A g ⁻¹)	HSC	42.15 Wh kg ⁻¹	852 W kg ⁻¹	88.46% (10,000 cycles)	[87]
Liquid-phase sulfidation	NiCo-S	2081 F g ⁻¹ (1 A g ⁻¹)	HSC	25.58 Wh kg ⁻¹	400 W kg ⁻¹	75.7% (5000 cycles)	[88]

4.3. MOF-Derived Ni/Co Phosphides and Phosphites Electrode Materials for SCs

Although sulfidation can improve the electrical conductivity and redox activity of NiCo-based derivatives, further regulation of the electronic structure provides another route to improve charge-transfer kinetics. In this context, phosphidation has emerged as an important derivatization strategy for NiCo-based materials. To systematically understand the structure formation and electronic transformation, recent progress in MOF-derived NiCo-phosphides is discussed below from the perspectives of gas-phase and liquid-phase phosphidation strategies.

Typically, gas-phase phosphidation utilizes solid phosphorus sources (e.g., NaH₂PO₂, KH₂PO₂, or red P) to react with NiCo-MOF precursors under inert atmospheres. These sources decompose to release highly reactive PH₃ gas at elevated temperatures, triggering a gas-solid topological reaction. During this process, the exposed Ni/Co nodes are fully phosphidated into bimetallic phosphides, while the organic ligands carbonize *in situ* to form an amorphous carbon matrix. Furthermore, the massive release of gases creates abundant mesopores and defects, which significantly accelerate the overall reaction kinetics of the SC electrodes. As a representative example, Wang et al. constructed hollow NiCoP@C(Zn) nanocuboids through sequential carbonization and gas-phase phosphidation of a Zn-containing NiCo-BTC MOF precursor. During carbonization at 950 °C, Zn species were volatilized and served as an *in situ* sacrificial pore-forming agent, generating abundant micropores while maintaining the original nanocuboid framework. Subsequent gas-phase phosphidation using NaH₂PO₂ converted the Ni/Co species into NiCoP nanoparticles embedded within the carbon matrix (Figure 4a). The synergistic effects of gas-phase phosphidation and Zn-mediated pore engineering resulted in a hierarchical hollow structure with abundant ~0.5 nm micropores, which facilitated multidirectional OH⁻ diffusion and shortened ion/electron transport pathways (Figure 4b–e). Consequently, the NiCoP@C(Zn) electrode achieved a specific capacitance of 1203 F g⁻¹ at 1 A g⁻¹, retained 82.8% capacitance at 15 A g⁻¹, and maintained 66.7% retention after 10,000 cycles [89]. To further advance the hierarchical structural design on metallic substrates, Qu et al. grew Ni-MOF nanosheets and Prussian blue analogue nanocubes on NF via a MOF-on-MOF strategy. Following gas-phase phosphidation using NaH₂PO₂·H₂O at 350 °C, the precursor film was converted into a Co₂P/Ni₂P heterostructure derivative. The multi-valence synergistic effects can accelerate charge transport and accommodate volume expansion, resulting in a remarkable capacity of 5124.2 mF cm⁻² at 1 mA cm⁻². In addition to template engineering, regulating the intrinsic MOF ligands provides another innovative pathway [90]. Cui et al. co-assembled a NiCoZn-MOF precursor using 5-aminotetrazole and 2-MeIm ligands to derive a nitrogen-doped carbon (NC) coated hollow spherical NiCoP through high-temperature carbonization and gas-phase phosphidation (Figure 4f). DFT calculations demonstrated that the massive NiCoP/NC interfaces effectively enhanced charge redistribution and reduced the OH⁻ adsorption energy to -3.91 eV. Consequently, the composite achieved a capacitance of 1551 F g⁻¹ at 1 A g⁻¹ and retained 83.7% after 8000 cycles at 5 A g⁻¹, enabling the assembled HSC to sustain a high energy density of 54.2 Wh kg⁻¹ at 11,948.9 W kg⁻¹ [91].

In parallel, liquid-phase phosphidation offers an appealing way for achieving precise morphological control under milder solvent conditions. For instance, Ding et al. synthesized ternary Ni-Co-P micro/nano-derivatives via a facile one-pot solvothermal strategy using NiCl₂·6H₂O, CoCl₂·6H₂O, and NaH₂PO₂·H₂O as reactants in a mixed solvent at 160 °C. The stoichiometric ratio (Ni/Co = 8:1) induced a strong synergistic effect between Ni and Co redox species, significantly facilitating the charge transfer kinetics. Electrochemical evaluations demonstrated that the liquid-phase derivative provided a high specific capacitance of 1448 F g⁻¹ at 1 A g⁻¹, while its corresponding asymmetric SC contributed a competitive energy density of 22.8 Wh kg⁻¹ [92]. Beyond utilizing external

phosphorus sources, exploring MOFs with multi-functional capabilities provides a brilliant route. Huang et al. tactfully developed plate-like phosphonate-based MOFs (Ni-PMOF) that served simultaneously as both the geometric template and the intrinsic phosphorus source. Upon a controlled in-situ liquid-phase conversion in a hexamethylenetetramine solution containing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 90 °C, the precursors were topotactically transformed into bimetallic phosphite nanosheet arrays (Ni/Co-POH-2). This unique open-framework architecture not only possessed superior conductivity but also maximized the exposure of accessible active surfaces, yielding a specific capacitance of 1905.6 F g^{-1} at 1 A g^{-1} and enabling the ASC to deliver an energy density of 36.59 Wh kg^{-1} [93]. To relieve framework collapse or complex recrystallization associated with elevated thermal treatments, Sui et al. developed a direct liquid-phase phosphidation strategy at room temperature (25 °C). By treating a NiCo-MOF template in a PCl_3 solution, they constructed a flower-like Co-Ni-B-P composite. The formation of metal-phosphorus bonds reduces the electronegativity of the material, thereby enhancing its electrochemical activity and accelerating ion transport, while the phosphating treatment modulates the electronic structure and facilitates electron conduction. Consequently, the prepared electrode delivered a specific capacitance of 1578 F g^{-1} at 1 A g^{-1} while the assembled asymmetric supercapacitor achieved a specific energy of 76.5 Wh kg^{-1} at a specific power of 849 W kg^{-1} [94].

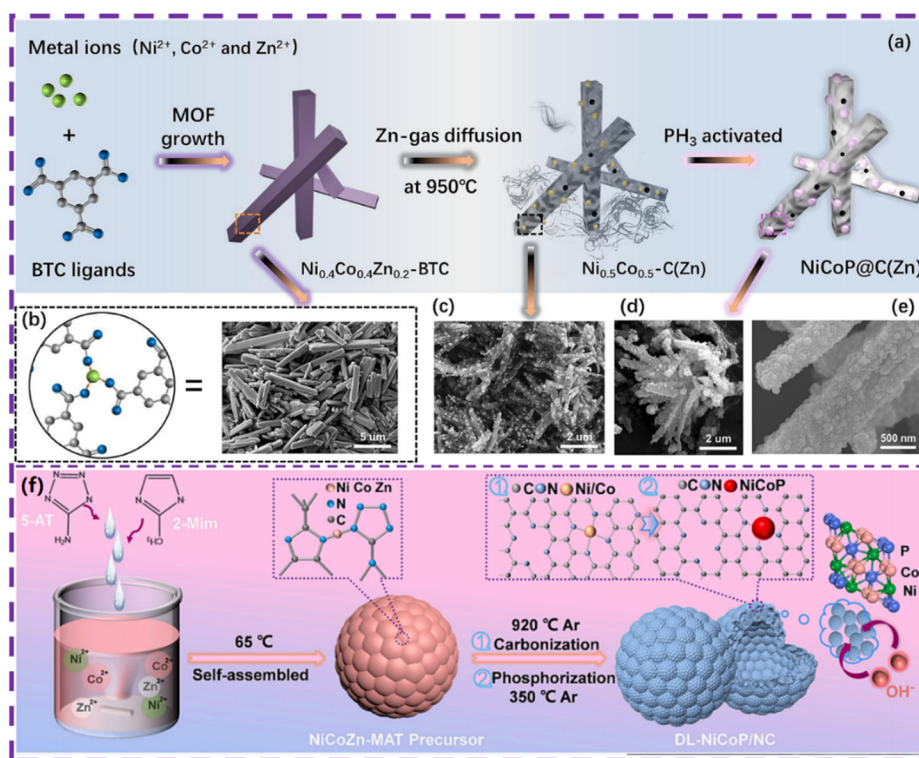


Figure 4. (a) Schematic diagram of the synthesis of 1D NiCoP@C(Zn) nano-cuboids. (b) The coordination molecules and FE-SEM image of the MOF precursor ($\text{Ni}_{0.4}\text{Co}_{0.4}\text{Zn}_{0.2}\text{-BTC}$). FE-SEM images of (c) $\text{Ni}_{0.5}\text{Co}_{0.5}\text{-C(Zn)}$ and (d,e) NiCoP@C(Zn) . Reproduced with permission [89]. Copyright 2023, Elsevier. (f) Schematic of the synthesis for hollow spherical DL-NiCoP/NC. Reproduced with permission [91]. Copyright 2023, Elsevier.

In summary, the development of NiCo-based phosphide and phosphite derivatives for supercapacitors advances through distinct gas- and liquid-phase pathways to overcome the kinetic limitations of pristine NiCo bimetallic oxides. Gas-phase phosphidation typically relies on high-temperature vapor-mediated reactions to induce topological reconstruction, leading to highly crystalline heterostructures with optimized electronic structures that facilitate surface redox kinetics. In contrast, liquid-phase strategies provide milder reaction environments, enabling better preservation of morphological fidelity during room-temperature or low-temperature conversion processes. Despite these advantages, the two approaches also present inherent trade-offs in terms of structural controllability, scalability, and processing complexity. Gas-phase routes often yield superior crystallinity and electronic coupling but require more demanding conditions, whereas liquid-phase methods offer greater synthetic flexibility at the expense of crystallinity or phase uniformity in certain systems. These MOF-derived phosphide materials generally benefit from enhanced electrical conductivity, porous architectures, and engineered heterointerfaces, which collectively promote ion/electron transport and mitigate volume variation during cycling.

However, their practical performance should be evaluated in a balanced manner considering not only electrochemical metrics but also synthesis feasibility and structural stability under long-term operation.

5. Functional Coatings in NiCo-Based Materials for SCs

The practical application of NiCo-based derivatives is often hindered by insufficient intrinsic conductivity at high rates and structural degradation (e.g., collapse or agglomeration) during high-temperature derivatization. Specifically, integrating highly conductive carbonaceous materials (e.g., graphene and CNTs) can establish continuous electron-transport networks and help buffer volume changes. Similarly, coupling with 2D MXenes can facilitate ion/electron transport and suppress precursor aggregation through interfacial confinement. In addition, combining NiCo-based materials with other transition-metal compounds provides opportunities to regulate heterointerfacial charge transfer and introduce additional redox-active sites. These multicomponent strategies therefore provide an effective approach to improving the electrochemical performance of NiCo-based electrodes.

5.1. Carbon Coating in NiCo-Based Materials for SCs

Carbon materials, owing to their exceptional intrinsic conductivity, chemical stability, and highly tunable spatial dimensions (ranging from 0D to 3D), have emerged as suitable conductive components for improving electrical transport and structural stability of NiCo-based derivatives. The multidimensional carbon matrix provides continuous conductive pathways for electron transport. Meanwhile, its spatial confinement and structural support can suppress the agglomeration and volume expansion of NiCo-based materials during repeated charge/discharge cycles, thereby improving the utilization of electroactive sites.

To address the intrinsically poor conductivity of NiCo-MOFs, integrating carbon quantum dots (CQDs) is a highly efficient microscopic modification strategy. For instance, Wang et al. introduced N-doped CQDs (CQD-CAN) into a NiCo-MOF precursor through a controlled hydrothermal method. The 0D CQDs established electron-rich regions and increased the electron cloud density around the active Ni and Co centers, thereby facilitating charge transfer. Benefiting from this optimized electronic structure, the NiCo-MOF@CAN composite presented a remarkable capacitance of 1917.7 F g^{-1} at 5 mV s^{-1} [95]. Beyond 0D dots, 1D multiwalled carbon nanotubes (MWCNTs) provide continuous conductive pathways and robust mechanical support. For example, Wang et al. synthesized a flower-string-like NiCo-MOF/MWCNT composite via a simple solvothermal approach. The incorporation of 1D carboxylated MWCNTs provided a highly conductive backbone that effectively guided the in-situ growth of 2D NiCo-MOF nanosheets. This specific interaction prevented the dense overstacking observed in pure hydrangea-like MOF microspheres, resulting in a well-dispersed hierarchical architecture. Benefiting from this morphological optimization and the synergistic conductive network, the composite delivered an enhanced specific capacitance of 1010 F g^{-1} at 0.5 A g^{-1} , alongside exceptional long-term stability with 100% capacitance retention after 3000 cycles at 5 A g^{-1} [60].

Reduced graphene oxide (rGO) nanosheets offer massive surface areas that can flexibly accommodate active materials. Salunkhe et al. anchored NiCo-MOF nanoflakes directly onto rGO sheets to form NiCo-MOF/rGO via a solvothermal method. In this hybrid architecture, the conductive rGO matrix effectively suppressed MOF agglomeration and maintained structural integrity, while the ultrathin MOF nanoflakes shortened ion diffusion paths. Driven by the synergistic effect between the bimetallic nodes and the rapid electron transport of rGO, the nanocomposite yielded an outstanding specific capacitance of 1320 F g^{-1} at 4 mA cm^{-2} , alongside a robust capacitance retention of 90.6% after 5000 cycles [96]. Additionally, 3D carbon materials (such as carbon aerogels and carbon foams) can serve as excellent composite matrices to overcome the inherent restacking issues of lower-dimensional carbons. For instance, Ghosh et al. constructed a binder-free composite of NiCo-MOF and a 3D carbon aerogel (CA) on flexible CC using a mild solution method. The CA inherently possesses an ultra-low density and an interconnected porous network, upon which NiCo-MOF nanoparticles are densely crystallized. This robust 3D architecture successfully provided continuous multi-directional electron transport superhighways and ensured fast ion penetration. Consequently, the composite electrode afforded a competitive gravimetric capacitance of 349 F g^{-1} at 2 mV s^{-1} , demonstrating its potential for flexible supercapacitor applications [97].

Collectively, these studies suggest that carbon coatings can mitigate several limitations of NiCo-MOFs by improving electrical transport, regulating morphology, enhancing structural stability, and increasing active-site accessibility. These findings provide useful guidance for the design of high-performance supercapacitor materials.

5.2. MXenes Coating in NiCo-Based Materials for SCs

Beyond carbon materials, 2D MXenes offer competitive properties for NiCo-based materials due to their metallic conductivity and abundant surface functional groups. However, their intrinsic tendency to restack and

weak interfacial bonding with active materials severely restrict electrolyte ion transport and structural stability. To release their full potential for advanced SCs, specialized structural and interfacial engineering strategies have been developed to circumvent restacking and strengthen electronic coupling [98,99]. Wang et al. employed a facile ultrasonic method to simultaneously exfoliate MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) and in-situ synthesize NiCo-MOF nanosheets. This strategy effectively prevented MXene oxidation and restacking, allowing the highly conductive MXene flakes to uniformly disperse on the MOF surface. The NiCo-MOF/ $\text{Ti}_3\text{C}_2\text{T}_x$ exhibited a high specific capacitance of 815.2 F g^{-1} at 1 A g^{-1} . Furthermore, the assembled ASC delivered a notable energy density of 39.5 Wh kg^{-1} at 562.5 W kg^{-1} , coupled with an 82.3% capacitance retention over 10,000 cycles at 5 A g^{-1} [100]. To intrinsically modulate the electronic structure and enlarge the interlayer spacing, Wei et al. prepared a 2D expanded MXene matrix using MgO as spacers, followed by the in-situ growth of NiCo-MOFs. During the formation process, the abundant surface -OH groups on the expanded MXene attracted metal ions via weak coordination. This interaction strategically induced surface oxygen defects, effectively compensating for the intrinsic shortcomings of the MOF. Electron paramagnetic resonance (EPR) spectroscopy confirmed the presence of these oxygen vacancies, while DFT calculations revealed a narrowed bandgap and enhanced OH^- adsorption, which could facilitate redox kinetics. Consequently, the defect-rich MXene@NiCo-MOF composite yielded a capacitance of 2078.1 F g^{-1} at 1 A g^{-1} , enabling its corresponding HSC to deliver 40.23 Wh kg^{-1} with 84.4% capacitance retention over 10,000 cycles [101]. Breaking conventional 2D limitations, Lao et al. transformed flake MXenes into 1D MXene-fibers via a KOH treatment to construct a $\text{Ni}(\text{Co})_3\text{S}_4$ @MXene-fibers composite through solvothermal sulfidation. The highly electronegative 1D fibers triggered robust electrostatic self-assembly with the bimetallic sulfides, uniformly anchoring the active nanoparticles. This 1D architecture not only prevented sulfide accumulation but also established a directed charge-transfer network. Boosted by maximized active site exposure and the rich redox reactions of the bimetallic centers, the electrode afforded a high specific capacitance of 829.4 C g^{-1} at 1 A g^{-1} . Ultimately, the assembled ASC showcased a high energy density of 63.3 Wh kg^{-1} at 850 W kg^{-1} , maintaining a good capacitance retention of 71.4% even after 20,000 cycles [102].

5.3. Metal Compounds Coating in NiCo-MOF for SCs

To maximize the electrochemical energy storage capability, heterogeneously compositing NiCo-based materials with other transition metal compounds (e.g., metal oxides, hydroxides) has emerged as an effective strategy. Distinct from the primarily physical support role of carbon-based matrices, the introduction of metal compounds aims to provide abundant redox-active sites by constructing heterojunction interfaces and built-in electric fields. This strategy can trigger robust electronic coupling and chemical synergistic effects among multi-metal centers, thereby contributing to improved energy-storage performance of SCs [103]. Beyond MOF-based composites, recent studies on related NiCo-LDH systems have also demonstrated the effectiveness of hierarchical metal oxide/hydroxide heterostructures. Berrabah et al. fabricated binder-free NiO/Ni(OH)₂-NiCo-LDH core-shell arrays via potentiostatic electrodeposition for flexible asymmetric supercapacitors. The NiO/NiCo-LDH electrode delivered a specific capacity of 940 C g^{-1} at 1 A g^{-1} with 94.2% retention after 5000 cycles, while the assembled ASC achieved an energy density of 13.4 Wh kg^{-1} at 148.3 W kg^{-1} [104]. For metal oxide coatings, Ji et al. prepared CuCo_2O_4 /NiCo-MOF nanoflake vertical arrays on NF by a self-sacrificial template method through a solvothermal process. Specifically, the acidic MOF ligands (PTA) released protons to partially etch the pre-synthesized CuCo_2O_4 oxide rods, simultaneously triggering the in-situ nucleation and directed growth of MOF nanoflakes, forming uniform fence-like CuCo_2O_4 /NiCo-MOF nanoflake arrays. This spinel CuCo_2O_4 provided multidirectional interconnected channels for rapid OH^- diffusion and prevented the stacking of MOF sheets. Driven by the strong interfacial synergistic effect, the fabricated electrode yielded an outstanding areal specific capacity of 12.81 F cm^{-2} at 2 mA cm^{-2} [105]. Similarly, focusing on structural regulation, Qing et al. synthesized robust NiCo molybdenum metal oxide (NCMO) nanoflowers via hydrothermal and calcination methods, followed by the directional in-situ growth of NiCo-MOF nanosheets, forming the NCMO@NiCo-MOF composite. The pre-formed NCMO acted as a highly conductive skeleton to guide the uniform anchoring of the NiCo-MOF. Supported by this hierarchical nanoflower skeleton, the composite effectively avoided the random aggregation of pristine MOF nanosheets and significantly expanded the electrolyte-electrode contact area. Consequently, the electrode afforded an impressive capacitance of 1724 F g^{-1} at 1 A g^{-1} . Furthermore, the corresponding ASC exhibited a peak energy density of 44.5 Wh kg^{-1} at 824.8 W kg^{-1} [106]. In parallel to utilizing complex mixed metal oxides (e.g., NCMO), conventional pseudocapacitive oxides like MnO_2 have also been skillfully employed as functional underlying substrates to synergistically upgrade NiCo-MOF materials. Li et al. deposited MnO_2 and NiCo-MOF on ACC via a stepwise synthesis strategy, forming a self-supported NiCo-MOF@ MnO_2 heterostructure with an overlapping massive nanostructure. This unique design addressed the volume expansion of MnO_2 and the low

intrinsic conductivity of the NiCo-MOF. In this composite configuration, the inner MnO_2 layer acts as a crucial bifunctional component: it not only provides supplementary pseudocapacitance but also serves as an active substrate that synergistically promotes the growth of the outer NiCo-MOF arrays. The optimized electrode exhibited an areal capacitance of 15.2 F cm^{-2} at 2 mA cm^{-2} , while the assembled ASC maintained a capacitance retention of 85.67% over 10,000 cycles at 80 mA cm^{-2} [107].

LDHs feature unique 2D lamellar structures and rich surface hydroxyl groups, enabling strong interfacial coupling with NiCo-MOFs. Utilizing 2D hydroxides as structural guides, Cheng et al. realized the *in situ* growth of NiCo-MOF through a two-step hydrothermal process (Figure 5a). This design can inhibit the restacking of hollow-structured MOFs by immobilizing them on flower-like nickel-molybdenum layered double hydroxide (NiMo-LDH) nanosheets (Figure 5b,c). The electroactive NiMo-LDH nanosheets not only provided a large accessible surface area with multiple active sites for MOF nucleation, but also participated in Faradaic redox reactions to impart additional capacitance. Benefiting from the NiMo-LDH@NiCo-MOF heterojunction, the hierarchical flower-like composite showcased a specific capacitance of 1536 F g^{-1} at 1 A g^{-1} (Figure 5d), empowering the assembled ASC to output a high energy density of 60.2 Wh kg^{-1} at a power density of 797 W kg^{-1} [108]. Beyond utilizing LDHs as electroactive substrates in composite systems, exploiting their intrinsic chemical reactivity as sacrificial templates presents another sophisticated paradigm for constructing NiCo-MOF/hydroxide heterostructures. For instance, Feng et al. constructed a 3D porous flower-like NiCo-MOF@Ni-LDH composite. They innovatively used LDH as a precursor to synthesize the NiCo-MOF, followed by a hydrothermal recombination with Ni-LDH. This sophisticated structure effectively integrated the high porosity of the MOF with the rapid redox kinetics of the hydroxide, resulting in a capacitance of 1880 F g^{-1} at 1 A g^{-1} [109].

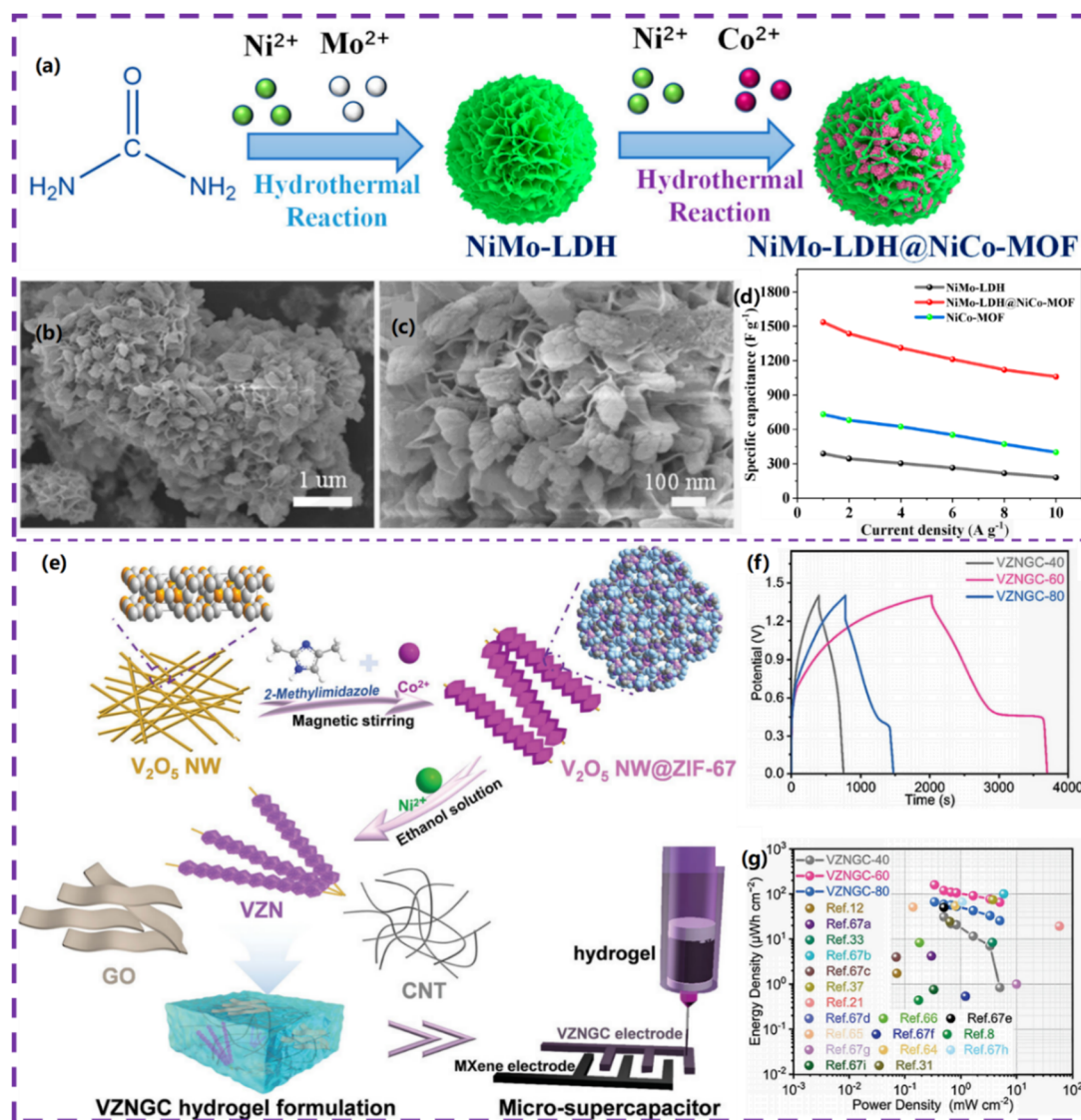


Figure 5. (a) Schematic diagram of the synthesis method for NiMo-LDH@NiCo-MOF. (b,c) SEM images of the NiMo-LDH@NiCo-MOF composite at different magnifications. (d) Specific capacitances of the NiMo-

LDH@NiCo-MOF, NiMo-LDH, and NiCo-MOF electrodes. Reproduced under the terms of the CC BY license from [108] under the terms of the Creative Commons Attribution (CC BY 4.0) license. (e) Schematic illustration of the preparation of VZN and schematic diagram of the 3D-printed micro-supercapacitor. (f) GCD curves of the as-fabricated VZNGC hydrogels at a current density of 0.48 mA cm^{-2} . (g) Ragone plot. Reproduced with permission [110]. Copyright 2023, Wiley-VCH.

Beyond traditional oxides and hydroxides, oxyhydroxides (e.g., CoOOH) can act as highly conductive and catalytically active intermediate layers to intrinsically bridge NiCo-MOFs and substrates. Zhou et al. grew dodecahedral ZIF-67 on hydrothermally synthesized V_2O_5 nanowires. Then, immersing this precursor in a Ni^{2+} -containing ethanol solution triggered a metal-ion exchange that in-situ generated a CoOOH bridging layer while doping Ni^{2+} into the framework to obtain a ternary NiCo-MOF@CoOOH@ V_2O_5 composite (Figure 5e). Driven by the structural incompatibility of the $\text{Ni}^{2+} \text{ d}^8$ electronic configuration and ZIF-67 crystal, a unique hollow architecture with spatially separated active sites was formed. As explicitly validated by synchrotron-based X-ray absorption fine structure (XAFS) spectroscopy, this precisely coordinated heterostructure profoundly accelerated interfacial charge transfer, enabling the fabricated 3D-printed micro-SC to deliver a high areal capacitance of 0.585 F cm^{-2} at 0.48 mA cm^{-2} (Figure 5f) and an outstanding Ragone performance (Figure 5g) [110]. Overall, combining NiCo-MOFs with metal compounds can effectively improve electrical conductivity, provide more electroactive sites, enhance structural stability, and accelerate ion and electron transport, thereby significantly boosting the capacitive performance of electrode materials.

Nevertheless, increasing compositional complexity does not necessarily translate into greater practical value. Functional coatings should therefore be evaluated not only by the resulting capacitance enhancement, but also by whether the added component provides a distinct interfacial or structural function sufficient to justify the additional synthesis steps, cost, and reproducibility challenges. To provide a direct comparison among the major engineering strategies discussed above, their principal advantages, limitations, synthesis complexity, scalability, and suitable device applications are summarized in Table 3.

Table 3. Comparison of major engineering strategies for NiCo-based materials in SCs.

Strategy	Main Benefits	Main Limitations	Synthesis Complexity	Scalability	Device Configuration	Representative Performance
Morphology control	More active sites; shorter ion pathways	Limited conductivity improvement; reproducibility issues	Low-moderate	Moderate-high for simple routes; route-dependent otherwise	ASC/HSC; flexible SCs	1126.7 F g^{-1} at 0.5 A g^{-1} [9]
Self-supporting architectures	Binder-free; low resistance; high loading	Substrate dependence; large-area uniformity	Moderate	Moderate; substrate/growth dependent	Flexible/wearable, high-loading SCs	53.6 F cm^{-2} at 1 mA cm^{-2} ; loading: 23.3 mg cm^{-2} [41]
MOF-derived oxides/hydroxides	Improved structural stability; rich redox activity	Pore collapse; moderate conductivity	Moderate	Moderate; thermal conversion required	ASC/HSC; self-supported electrodes	1971.4 F g^{-1} at 1 A g^{-1} ; 92.85% after 5000 cycles [68]
MOF-derived sulfides	Enhanced conductivity; rich redox activity	Structural stability; extra sulfidation	Moderate-high	Moderate; sulfidation-dependent	ASC/HSC; wearable devices	2392 F g^{-1} at 1 A g^{-1} ; HSC: 30.1 Wh kg^{-1} at 800.2 W kg^{-1} [79]
MOF-derived phosphides/phosphites	Enhanced conductivity; fast charge transfer	Complex conversion; demanding conditions	Moderate-high; route-dependent	Route-dependent; lower for gas-phase routes	High-rate devices; ASC/HSC	1905.6 F g^{-1} at 1 A g^{-1} [93]
Functional coatings	Improved conductivity and interface stability	Added fabrication complexity	Moderate-high; route-dependent	Route-dependent	Flexible devices; ASC/HSC	1724 F g^{-1} at 1 A g^{-1} ; ASC: 44.5 Wh kg^{-1} at 824.8 W kg^{-1} [106]

Note: The listed values are representative results from the studies reviewed herein rather than directly comparable performance ranges. Electrochemical metrics are retained using the normalization basis reported in the original studies; therefore, gravimetric, areal, and capacity-based values should not be directly compared across different normalization formats. Scalability is qualitatively assessed based on synthesis complexity, processing conditions, substrate requirements, and additional conversion steps reported in the reviewed studies.

Overall, no single strategy is universally optimal for NiCo-based supercapacitors. Morphology control provides a relatively simple foundation for improving active-site accessibility but cannot fully address intrinsic conductivity limitations. Self-supporting architectures appear to offer a favorable balance for practical device deployment because they eliminate binders, reduce interfacial resistance, and accommodate high active-material

loading, although substrate cost and large-area uniformity remain important considerations. MOF derivatization further improves electrical transport and structural robustness, with oxides/hydroxides generally offering greater processing simplicity, while sulfides and particularly phosphides involve additional conversion steps and more demanding processing conditions. Functional coatings enable further interfacial optimization but introduce additional materials and fabrication steps. Therefore, relatively simple morphology-control routes and direct-growth self-supporting architectures appear more amenable to scale-up, while practical strategy selection should balance electrochemical performance, scalability, and cost-effectiveness.

6. Conclusions and Perspectives

6.1. Conclusions

NiCo-based materials have attracted considerable attention for high-performance supercapacitors because of their rich redox chemistry and tunable structural characteristics. The studies reviewed herein demonstrate that different engineering strategies address distinct performance limitations. Morphology control can improve active-site accessibility and shorten ion-transport pathways, while self-supporting architectures reduce interfacial resistance, eliminate binders, and enable higher active-material loading. Through appropriately controlled thermal or chemical conversion, NiCo-MOFs can be transformed into oxides, hydroxides, sulfides, and phosphides, with the hierarchical porous features of the precursor retained to varying degrees while electrical conductivity and electrochemical reactivity can be improved. However, the extent of structural preservation and performance enhancement depends strongly on the derivative composition and specific conversion conditions. Functional coatings can further regulate interfacial charge transfer and structural stability through multicomponent interactions.

However, these strategies involve different limitations and trade-offs. Morphology regulation provides a relatively simple structural optimization route but cannot fully overcome intrinsic conductivity limitations. Self-supporting architectures appear favorable for practical electrode construction, although substrate cost and large-area uniformity remain important considerations. Sulfide and phosphide derivatization can provide favorable charge-transfer kinetics but generally involves greater conversion complexity, whereas functional coatings introduce additional materials and fabrication steps. Therefore, no single strategy is universally optimal. A more promising direction is the rational integration of complementary approaches, particularly controlled morphology, self-supporting architectures, and mild derivatization or interfacial engineering, while simultaneously considering conductivity, mass loading, cycling stability, synthesis complexity, and device-level applicability.

6.2. Perspectives

Despite the substantial progress in the development of diverse NiCo-based materials, several critical challenges remain before their large-scale commercialization. Therefore, future studies should prioritize the following key aspects:

(1) New ligand engineering and surface modification techniques must be further explored to alleviate the poor conductivity and structural collapse of NiCo-based materials. By introducing highly conductive components to construct multi-dimensional conductive networks and utilizing lattice defect engineering to fortify coordination bonds, the electron/ion transport kinetics and structural durability of the NiCo-based electrodes can be concurrently optimized.

(2) Mild conversion strategies should be developed to address the problems (such as pore collapse, loss of active sites, and uncontrollable morphological agglomeration) that occur during severe MOF derivation and etching processes. Under mild reaction conditions, mesoporous networks and defect sites can be successfully introduced while preserving, to a greater extent, the geometric features of the precursor, achieving the appropriate balance between conductivity enhancement and active site exposure.

(3) Advanced in-situ/operando characterization techniques, such as in-situ XRD, Raman spectroscopy, and XAFS, should be further employed to monitor phase transformations and coordination-environment evolution of NiCo-based electrodes during cycling. Meanwhile, systematic failure analysis should be strengthened to identify structural collapse, active-material detachment, and interfacial degradation. Combining dynamic characterization with post-cycling analysis can provide deeper insight into energy-storage and degradation mechanisms.

(4) AI- and machine-learning-guided material design should be further integrated into the development of NiCo-based electrodes. By establishing structure-property relationships among composition, morphology, synthesis conditions, and electrochemical performance, data-driven models may assist in screening promising materials and optimizing synthesis parameters, thereby reducing empirical trial-and-error and accelerating the rational design of high-performance NiCo-based electrodes.

(5) Practical device evaluation and scalable fabrication should receive greater attention. Future studies should consider high active-material loading, areal and volumetric performance, electrode charge balancing, electrolyte

compatibility, and long-term stability under realistic operating conditions. In particular, the compatibility of NiCo-based electrodes with different electrolyte systems, including aqueous, organic, and ionic-liquid electrolytes, should be systematically evaluated in terms of ion transport, electrochemical stability window, and operating voltage.

In summary, NiCo-based materials have demonstrated great potential for advanced SCs owing to their high theoretical capacitance and rich redox chemistry, with significant current achievements explicitly realized in morphology regulation and heterostructure construction. Moving forward, future studies on NiCo-based electrodes can prioritize the interfacial compatibility and synergistic effects among diverse active components, conductive substrates, and electrolytes. Elucidating corresponding electrochemical mechanisms through state-of-the-art characterization techniques and the continuous development of multidimensional structural designs are essential. Advanced *in situ* characterization methods can provide deeper insights into charge-transfer processes and structural evolution, while DFT simulations integrated with machine learning enable the targeted design of functional heterojunctions with rapid ion transport and good structural integrity, accelerating the transition from fundamental research to commercial applications for high-energy and long-term NiCo-based materials in high-performance SC.

Author Contributions

S.Z.: Conceptualization, Data curation, Formal analysis, Investigation, Writing—original draft. T.W.: Investigation, Resources, Writing—original draft. T.Z.: Visualization, Formal analysis. H.C.: Data curation, Formal analysis. D.S.: Conceptualization, Funding acquisition, Supervision. T.M.: Writing—review & editing, Supervision, Funding acquisition. All authors have read and agreed to the published version of the manuscript.

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No new data were created or analyzed in this study.

Conflicts of Interest

Given the role as an editorial board member, Dong Shu had no involvement in the peer-review of this paper and had no access to information regarding its peer-review process. Full responsibility for the editorial process of this paper was delegated to another editor of the journal.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

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