Recent Research of NiCo$_2$O$_4$/Carbon Composites for Supercapacitors

Junming Xu $^1$, Yang Shi $^1$, Jipeng Cheng $^2$,* and Xinchang Wang $^3$

$^1$ College of Electronic Information, Hangzhou Dianzi University, Hangzhou 310018, China; xujunming@hdu.edu.cn (J.X.); shiyang10022022@163.com (Y.S.)
$^2$ School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China
$^3$ School of Physics and Microelectronics, Zhengzhou University, Zhengzhou 450052, China; wxclhm@zzu.edu.cn
* Correspondence: chengjp@zju.edu.cn

Abstract: Supercapacitors have played an important role in electrochemical energy storage. Recently, researchers have found many effective methods to improve electrode materials with more robust performances through the increasing volume of scientific publications in this field. Though nickel cobaltite (NiCo$_2$O$_4$), as a promising electrode material, has substantially demonstrated potential properties for supercapacitors, its composites usually show much better performances than the pristine NiCo$_2$O$_4$. The combination of carbon-based materials and NiCo$_2$O$_4$ has been implemented recently due to the dual mechanisms for energy storage and the unique advantages of carbon materials. In this paper, we review the recent research on the hybrids of NiCo$_2$O$_4$ and carbon nanomaterials for supercapacitors. Typically, we focused on the reports related to the composites containing graphene (or reduced graphene oxide), carbon nanotubes, and amorphous carbon, as well as the major synthesis routes and electrochemical performances. Finally, the prospect for the future work is also discussed.

Keywords: nickel cobaltite; composites; supercapacitors; graphene; carbon nanotubes

1. Introduction

Supercapacitors, also called electrochemical capacitors, are deemed as a kind of bridging candidate between batteries and conventional capacitors due to the unique features of high-power density, excellent safety, easy maintenance, and long lifespan [1]. They are urgently expected to have high-energy density to store more energy for sustainable applications and are even to expected to be substitutes for re-chargeable batteries. However, it is a rather challenging issue. An important feature for supercapacitors is the high-specific capacitance ($C_m$, $C_m = Q/V$, where $Q$ and $V$ are amounts of stored charge and potential window, respectively. Energy density ($E$) and power density ($P$) are also two important parameters for supercapacitors, and they can be expressed as the following two equations, $E = 0.5 \times C_m V^2$ and $P = E/(\Delta t)$, where $\Delta t$ is the discharge time, and $V$ is the potential window. Meanwhile, it is well known that the basic performances of a supercapacitor are basically determined by the electrode materials, in addition to the assembly manner and electrolytes. Thus, high-performance electrode materials have been deeply and widely investigated.

Based on the charge storage mechanism, supercapacitors can be classified into two kinds, i.e., pseudocapacitors (or redox-capacitors) and electrochemical double-layer capacitors (EDLCs) [2,3]. There are Faradic reactions occurring on the surface of the former one, while physical accumulation of double layer of charges forms at the interface of electrodes and electrolytes for EDLCs. Carbon-based materials with large surface areas are EDLC electrode materials. Thus, they show remarkably different behavior during the charge storage processes from pseudocapacitive materials. Redox-capacitors usually have high...
specific capacitances, about 10–100 times more than those of EDLCs but are restricted by the poor conductivity, leading to limited rate capability and cycle stability. The electrodes of EDLC are commonly carbon materials with high-surface areas, and they have better rate performances and more stable behavior than redox capacitors [4].

It is well known that only one type of electrode materials cannot meet the high requirements of supercapacitors. Recent research has found that the composites consisting of EDLC-based materials and transition metal oxides that store energy by reversible Faradaic reactions have outstanding capacitive behavior. The popularly investigated EDLC materials are activated carbon, graphene or reduced graphene oxide (rGO), and carbon nanotubes (CNTs) due to the high conductivity and large specific surface areas. Transition metal oxides include MnO₂ [2,5], Co₃O₄ [6], NiO [7], CoO [8], NiCo₂O₄ [9], Fe₂O₃ [10], etc. that have abundant sources with high-specific capacitances. Compared with others, binary metal oxide, NiCo₂O₄, showed better performances due to its higher activity and conductivity (2 × 10⁻² S cm⁻¹). It has mixed valence states of cations that can offer rich redox chemistry.

In 2010, Hu and co-workers broke new ground on using NiCo₂O₄ as an electrode material for supercapacitors [11]. It has a spinel structure and can offer large capacitance with low cost and good safety, showing an effective and satisfactory perspective as electrodes. There have been many review papers published related to NiCo₂O₄ and its composites for supercapacitor electrodes [12,13]. The conventional preparation methods of spinel NiCo₂O₄ include hydrothermal, electrochemical deposition, sol-gel, etc. NiCo₂O₄ nanostructures with various morphologies have exhibited excellent supercapacitive performances due to the existence of multiple redox couples of Co³⁺/Co²⁺ and Ni³⁺/Ni²⁺ [12]. Oxygen vacancies [14] and metal doping [15] in NiCo₂O₄ can adjust the electronic structure to enhance conductivity where intriguing methods are usually involved. In the redox reactions, NiCo₂O₄ materials with a single structure usually show limited kinetic characteristics because of the small surface area and low conductivity. Pristine NiCo₂O₄ with various nanostructures still suffers from certain drawbacks, such as capacitance fading and unsatisfied rate capability, because of the sluggish reaction kinetics under high-current densities. Thus, a reasonable design by integrating carbon nanomaterials with NiCo₂O₄ is figured out and implemented where the synergistic effects between two components have sustainable improvement for electrochemical performances.

There have been many reports related to the supercapacitive performances of NiCo₂O₄-based composites [16–19]. Among them, the hybrids of NiCo₂O₄ and carbon materials, including graphene, CNTs, and amorphous carbon, have exhibited considerable potential where the total conductivity is enhanced by graphitic crystalline carbon materials, and NiCo₂O₄ can guarantee a high-specific capacitance. Both EDLC and Faradic storage mechanisms participate in energy storage. Though there have been substantial numbers of review papers related to NiCo₂O₄ and its composites for supercapacitor application [20–22], a special review paper on the composites of NiCo₂O₄ and carbon is also necessary. In the present manuscript, the recent development of NiCo₂O₄/carbon hybrids as efficient electrode materials towards supercapacitors is concerned. This review will focus on the hybrids consisting of NiCo₂O₄ and graphene (rGO), CNTs or amorphous carbon, as well as their electrochemical performances and synthesis methods.

2. Composites of NiCo₂O₄ and Graphene

Graphene (or rGO) is a new type of 2D monolayer carbon structure that has a large theoretical specific area, high conductivity, and excellent mechanical strength. Pure graphene are easy to stack densely to form graphite by Van der Waals force, which significantly suppresses its practical application. However, the integration of guest materials will keep the graphene layers from stacking and make more surface area available to contact electrolytes. Thus, it is an ideal candidate to combine with guest materials to result in robust electrochemical properties [23]. Wang et al. [24] first reported the synthesis of NiCo₂O₄/graphene for supercapacitors, and the composite exhibited an initial specific capacitance of 835 F g⁻¹ at 1 A g⁻¹. At present, researchers have carried out much effort to prepare various compos-
ites containing graphene, such as powder materials, flexible films, graphene aerogel, etc. In this section, we will summarize the recent work on the composites of NiCo$_2$O$_4$/graphene for supercapacitors. According to the state of products, power composites and hybrid films will be discussed separately herein.

2.1. Powder Composites

The composites of NiCo$_2$O$_4$/graphene in powder state are commonly reported, and they can be easily synthesized by conventional routes, such as the hydrothermal method and calcination. Salarizadeh et al. [25] reported that the charge transfer resistance of NiCo$_2$O$_4$/rGO was about 7.6 times lower than that of pure NiCo$_2$O$_4$. To overcome the intrinsic disadvantages of pristine NiCo$_2$O$_4$ electrode, graphene and rGO have been employed to couple with NiCo$_2$O$_4$ for increasing the surface area, the wettability of the surface, and the electric conductivity [26–30]. In addition to rGO, multilayered graphene, fluorinated rGO, N-doped rGO [31], graphene quantum dots, and porous graphene aerogel [32] with different elements and various sizes have been involved to combine with NiCo$_2$O$_4$ to obtain electrode materials.

A series of hybrids of NiCo$_2$O$_4$ micro-shrubs and rGO were prepared by urea-assisted hydrothermal route by adjusting the amount of rGO [33]. The optimized one had good activity for oxygen reduction reaction and specific capacitance of 1305 F g$^{-1}$ at 5 mV s$^{-1}$ due to its better synergistic effect between two materials. After spray drying aqueous colloidal suspension of GO containing NiCo$_2$O$_4$ at high temperatures, NiCo$_2$O$_4$/rGO microspheres were synthesized, and the composite had a specific capacitance of 702 F g$^{-1}$ at 0.5 A g$^{-1}$ [34]. Similarly, Yuan et al. [35] applied the spray-assisted, self-assembly method to fabricate NiCo$_2$O$_4$ anchored on crumpled graphene microspheres, and the composite displayed a specific capacitance of 369.8 F g$^{-1}$ at 1 A g$^{-1}$.

Honeycombed-like NiCo$_2$O$_4$ nanosheet arrays consisting of ultrathin mesoporous nanosheets could be interdigitated vertically on the rGO surface on both sides, as displayed in Figure 1, and the composite exhibited considerable specific capacitance of 1380 F g$^{-1}$ at 1 A g$^{-1}$ [36]. In the materials preparation process, citric acid played an important role in inhibiting severely homogeneous nucleation and self-aggregation of metal precursors.

![Figure 1. Schematic synthesis strategy of the honeycombed-like hierarchical nanosheet array composites NiCo$_2$O$_4$/rGO. Reproduced with permission from [36]. Copyright 2020, Elsevier.](image-url)
Amorphous carbon spheres coated by multilayered graphene were combined with NiCo$_2$O$_4$ by hydrothermal, and the largest specific capacitance was tested about 920 F g$^{-1}$ at 1 A g$^{-1}$ [37]. The weight ratio of carbon spheres to NiCo$_2$O$_4$ had an obvious effect on the electric and ionic conductivity of composites. Petal-like NiCo$_2$O$_4$/rGO hybrids also showed dependence of electrochemical properties on the rGO weight contents [38]. Thus, previous reports demonstrated that the content of carbon materials in the composite has an effect on the electrochemical performances.

The doping of nitrogen atoms can substantially enhance the performances of graphene in the applications, such as supercapacitors, owing to the enhanced polarity of surface and electric conductivity. The pyrrolic nitrogen atoms can especially endow excellent electronic properties for graphene [39]. Hybrids of NiCo$_2$O$_4$/N-rGO had large specific capacitance and high activity as electrode materials for supercapacitors [40]. Paliwal et al. [41] partially wrapped N-doped rGO on NiCo$_2$O$_4$ by hydrothermal and calcination, and the hybrid delivered a high-specific capacitance. When it was combined with Bi$_2$O$_3$ electrode to make an asymmetric capacitor, it showed better performances than pristine NiCo$_2$O$_4$. However, the asymmetric capacitors showed a rather low Coulombic efficiency.

Fluorinated rGO was also involved to prepare NiCo$_2$O$_4$-based hybrids. In fluorinated rGO, fluorine atoms are covalently functionalized on the carbon skeleton. It has been extensively applied in energy conversion devices due to the excellent stability and amplified electrochemical reactivity. A composite of fluorinated rGO/NiCo$_2$O$_4$ nanorod was synthesized via a two-step hydrothermal method combined with the thermal-annealing process [42]. Fluorinated rGO could hinder the aggregation of NiCo$_2$O$_4$ nanorods, providing a conductive matrix for electron transportation. The composite showed high-specific capacitance (1356 F g$^{-1}$ at 1 A g$^{-1}$) and good cycle stability (remained 91% capacity after 3000 cycles at 5 A g$^{-1}$).

Graphene quantum dots (GQDs) are of single or few layer graphene with a tiny size of only several nanometers, much smaller than graphene. GQDs have novel chemical and physical properties of both graphene and quantum dots. Tremella-like NiCo$_2$O$_4$ could be homogeneously coated by GQDs, and the π-conjugated core with abundant edge sites from the GQDs made NiCo$_2$O$_4$ favorable for electric energy storage [43]. The composite exhibited a specific capacitance of 1242 F g$^{-1}$ at 30 A g$^{-1}$. Kharangarh et al. [44] deposited GQDs on NiCo$_2$O$_4$ by hydrothermal route and the hybrid displayed a specific capacitance of 471.4 F g$^{-1}$ at 0.35 A g$^{-1}$ in 0.1 M KOH.

2.2. Film Electrodes

The hybrid electrode material of NiCo$_2$O$_4$/graphene can also be synthesized onto some solid conductive substrates. Thus, it can be applied as an electrode directly without using any binder to avoid “dead surface” and conductive additives. In these cases, the performances of electrode materials are usually superior to those of powder materials [45] because they can fully exert the synergistic effect of graphene and NiCo$_2$O$_4$ without disturbance from binder and additives.

Nickel foam is an ideal conductive substrate to support rGO due to its low cost and 3D porous structure where rGO can fill up the voids in nickel foam. Feng et al. [46] electrodeposited NiCo$_2$O$_4$ nanoflakes onto the surface of rGO@Ni foam to improve the accessible electrode surface area. The composite electrode had a specific capacitance of 3.84 F cm$^{-2}$ at 2 mA cm$^{-2}$ and 71.6% retention at 50 mA cm$^{-2}$. The electrode could supply a flexible and strong scaffold to alleviate the brittle of NiCo$_2$O$_4$ nanoflakes during long-term work. Wei et al. [47] fabricated rGO-modified NiCo$_2$O$_4$/NiCo$_2$O$_4$ nanorods on nickel foam by hydrothermal synthesis and annealing. The presence of GO influenced the final morphology of metal oxide arrays and led to self-assembled nanoneedles, giving a high capacity of 1439 C g$^{-1}$ [47]. Hybrids of NiCo$_2$O$_4$/rGO on nickel foam were also prepared by CTAB-assisted hydrothermal synthesis following annealing and it was found that the GO content had effects on the electrochemical properties [48]. Lv et al. [49] deposited NiCo$_2$O$_4$/rGO on nickel foam by hydrothermal and the hybrid had a large specific surface
area of 108 m² g⁻¹ for supercapacitors. Recently, Shi et al. [50] applied a facile one-step ultrasonic spray to coat the hybrid of NiCo₂O₄/rGO on nickel foam, and it was directly used as the binder-free electrodes for supercapacitors.

In addition to nickel foam, carbon fibers are also used as a current collector to support electroactive materials due to the high conductivity and low weight [51]. For example, Patil et al. [52] prepared NiCo₂O₄ nanorod arrays on 2D rGO that was deposited on carbon fibers by a dip-dry process. Then, rGO could lead to a reduced interfacial resistance between carbon fibers and NiCo₂O₄ owing to the excellent electric conductivity. The hybrid electrode displayed a specific capacity of 458.3 mAh g⁻¹ at 3 mA cm⁻². This kind of electrode is usually flexible and can build solid-state supercapacitors easily. Hierarchical rGO-decorated NiCo₂O₄ nanowires were constructed on carbon fibers by a two-step hydrothermal route [53]. As supercapacitor electrodes, it delivered a specific capacitance of 1178 F g⁻¹ at 1 A g⁻¹ and 93.4% retention even at 10 A g⁻¹.

In the above cases, the composite films are anchored on some conductive substrates, such as nickel foam and carbon fibers. However, 3D porous architectures made up of graphene can also play this role to prepare binder-free electrodes. Since nitrogen atoms can offer lone-pair electrons which can enhance the fluidity and conjugation of electrons, the conductivity of N-doped graphene can be improved. 3D N-doped graphene frameworks derived from melamine sponge could support NiCo₂O₄ nanosheets to form a hierarchical structure [54]. It had a specific capacitance of 1198 F g⁻¹ at 1 A g⁻¹. Similarly, Wang et al. [55] deposited NiCo₂O₄ nanoparticles on 3D N-doped graphene inherited from melamine sponge as binder-free electrodes. It had a specific capacitance of 1576.5 F g⁻¹ at 1 A g⁻¹ because N-doping changed the surface wettability and electron distribution. The 3D holey graphene skeleton provided anchoring sites and stably confined NiCo₂O₄ nanowires on their inner surfaces, as shown in Figure 2. In Figure 2a, a 3D honeycomb-like structure composed of interconnected graphene is formed. After coating NiCo₂O₄ nanowires, they are uniformly distributed and anchored vertically throughout the 3D skeleton, as shown in Figure 2b. The holes on the 3D graphene offered an ion/electron transport pathway for longitudinal transport. Thus, the films could manifest a specific capacitance of 1118 F g⁻¹ at 1 A g⁻¹, as reported by Jiang et al. [56].

![Figure 2. SEM images of (a) 3D graphene and (b) graphene/NiCo₂O₄. Reproduced with permission from [56]. Copyright 2022, Elsevier.](image-url)
Zhou et al. [57] prepared 3D porous rGO/NiCo$_2$O$_4$ films by a Cu$_2$O template-assisted route, followed by calcination in which NiCo$_2$O$_4$ was embedded and made well dispersity of graphene, as shown in Figure 3. The porous free-standing films could afford 3D architectures, storing many electrolytes and serving as electrodes directly. It had specific capacitance of 708 F g$^{-1}$ at 1 A g$^{-1}$, showing good rate retention and stability (94.3% after 6000 cycles).

![Figure 3](image_url)

**Figure 3.** (a) Digital image (b,c) surface and cross-section SEM images of 3D rGO/NiCo$_2$O$_4$ film, (d) XRD patterns, and (e,f) TEM images of 3D rGO/NiCo$_2$O$_4$. Reproduced with permission from [57]. Copyright, 2020, Elsevier.

### 3. Composites of NiCo$_2$O$_4$ and CNTs

In general, the presence of carbon materials in NiCo$_2$O$_4$-based hybrids can accelerate the electron transfer and increase the surface area. CNTs are 1D structured crystalline carbon materials, possessing superior conductivity and chemical stability, as well as capacitive performances. Different from graphene, pure CNTs are prone to interconnect to each other to build a conductive network, and they can be used as a supporter and current collector [58]. However, the specific capacitance of pure CNTs is usually rather lower than activated carbon due to the limited specific surface area. Lee et al. [59] first reported that the hybrid of NiCo$_2$O$_4$/single-walled CNTs had a high-specific capacitance and excellent cycling stability. Hybrids of CNTs/NiCo$_2$O$_4$ were then researched widely. The supercapacitive performance of NiCo$_2$O$_4$@CNTs was theoretically studied by its structural and electronic properties using density functional theory predictions [60], showing improved density of states near the Fermi level and increased quantum capacitance. This section will discuss the hybrids of NiCo$_2$O$_4$/CNTs.

In Section 2, the composites of NiCo$_2$O$_4$/graphene are mostly prepared using GO as a precursor because there are abundant functional groups, such as hydroxy (–OH) and carboxyl (–COOH), on the surface. These groups act as anchoring sites to immobilize NiCo$_2$O$_4$. The hydrophilic surface of electrode materials is also very important for electrochemical reactions. For example, Wang et al. reported [61] that a small amount of
highly hydrophilic carbon dots decorated on the NiCo$_2$O$_4$ nanowire surface could make the surface more hydrophilic and easier for aqueous electrolyte infiltration. Meanwhile, the electrical conductivity of carbon dot/NiCo$_2$O$_4$ was 3.65 S m$^{-1}$, about 30-fold higher than that of NiCo$_2$O$_4$. For CNTs, the surface treatment is usually necessary for the attachment of guest metal oxides [62].

3.1. Powder Composite Materials

Due to the high conductivity of CNTs, the formation of core-shell structures with CNT as the core and pseudocapacitive materials, such as NiCo$_2$O$_4$, as the shell has been reasonably adopted to enhance the electrochemical performances. The CNT core can ensure the transportation of electrons, giving a low resistance and high strength to support the shell. Core/shell-like hybrids of NiCo$_2$O$_4$-decorated CNT could be prepared by a dry synthesis technique, and the size of NiCo$_2$O$_4$ nanoparticles was about 6 nm [63]. The core-shell hybrids exhibited a specific capacitance about 822 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$. Geng et al. [64] found that serious surface treatment of CNTs was detrimental to the structure and electrochemical properties of the composites. Ultrafine NiCo$_2$O$_4$ nanoparticles formed a uniform and continuous cladding on CNTs that was acid treated for 12 h, as shown in Figure 4a (sample NiCo$_2$O$_4$/CNT-12), while NiCo$_2$O$_4$ nanoparticles grew bigger on CNTs that were treated for 24 h (sample NiCo$_2$O$_4$/CNT-24), as in Figure 4b. The particle aggregation was ascribed to the increase of acid treatment time that formed more defects and functional groups on the CNT surface, inducing a larger amount of adsorption sites for metal ions, facilitating the growth of particles [65]. The composite with smaller particles had a higher specific capacitance of 828 F g$^{-1}$ at 1 A g$^{-1}$.

![Figure 4. SEM images of different materials, (a) NiCo$_2$O$_4$/CNT-12, The red dotted circles show the interspaces existing between NiCo$_2$O$_4$ nanoparticles; (b) NiCo$_2$O$_4$/CNT-24. Reproduced with permission from [64]. Copyright 2016, Wiley.](image-url)
To improve the interaction force between NiCo$_2$O$_4$ and CNTs, some special directing agents are employed in the synthesis process, such as deoxyribonucleic acid (DNA) and epoxy-ended hyperbranched polymer (EHP). Xue et al. [66] reported that DNA could wrap the CNT surface and prevent the aggregation through the repulsion between negatively charged DNA side chains and that DNA controlled the formation of NiCo$_2$O$_4$ nanoparticles around the CNTs via the strong electrostatic forces, resulting in uniform distribution of nanoparticles on the CNTs [66]. The resultant composites showed 760 F g$^{-1}$ at 5 mV s$^{-1}$. Hu et al. [67] used an EHP as the reactive template to in-situ prepare porous NiCo$_2$O$_4$ on a film of pristine CNTs. It possessed a better electrochemical performance in comparison to pure NiCo$_2$O$_4$ without CNTs.

Similar to graphene, N-doped CNTs were also involved to prepare NiCo$_2$O$_4$ composites. SnO$_2$/NiCo$_2$O$_4$/N-doped CNTs were prepared by a thermal reduction process, and it showed a specific capacitance of ~728 F g$^{-1}$ at 1 A g$^{-1}$ due to the synergistic effect between oxygen-enriched metal ions and N-doped CNTs in the hybrid [68]. A nanstructured MnO$_2$/NiCo$_2$O$_4$@N-doped CNT hybrid electrode was prepared by the hydrothermal process, showing a specific capacitance of ~543 F g$^{-1}$ at 0.5 A g$^{-1}$ [69].

CNTs decorated by NiCo$_2$O$_4$ nanoparticles were successfully fabricated by a one-pot hydrothermal method together with a sequent-annealing treatment [70]. The surfaces of the CNTs were partially covered by NiCo$_2$O$_4$, which provided the composites with high conductivity and a large surface area. The composites had a specific capacitance of 1055 F g$^{-1}$ at 1 A g$^{-1}$. NiCo$_2$O$_4$/CNT as a hybrid electrode material was synthesized by a the sonochemical method, and it exhibited high-specific capacitance 418.1 F g$^{-1}$ at 2 A g$^{-1}$ [71]. Recently, Cheng et al. [72] found that the annealing time of metal hydroxides on CNTs in air could affect the final morphology of the product. Elongated annealing time led to the transformation of NiCo$_2$O$_4$ from thin nanosheets to large nanoparticles. Nanoparticles on CNTs exhibited better electrochemical performances than nanosheets due to the close contact, about 1735 F g$^{-1}$ at 1 A g$^{-1}$. The annealing atmosphere also had an influence on the phase of metal oxide [73]. NiCo$_2$O$_4$ would form in nitrogen gas due to the reductive effect from CNTs at elevated temperatures, and it also had a high-specific capacitance of 1587 F g$^{-1}$ at 1 A g$^{-1}$.

3.2. Film Electrodes

The composites of NiCo$_2$O$_4$/CNTs could also be deposited on conductive substrates to prepare film electrodes directly. Due to the highly dispersive features and absence of a binder, the hybrid film electrodes often manifest a larger specific capacitance than power composites. Nickel foam is also an ideal substrate to support NiCo$_2$O$_4$/CNTs composites as a binder-free electrode [74]. The preparation methods include in-situ growth, arc thermal excitation, and the electrophoretic method. For example, coiled CNTs in situ grown on nickel foam were employed to coat NiCo$_2$O$_4$ nanosheets by the solvothermal method, and the binder-free electrode exhibited a specific capacitance of 2821 F g$^{-1}$ at 1 A g$^{-1}$ [75]. The porous feature of NiCo$_2$O$_4$ nanosheets and the 3D architecture could increase the number of electroactive sites effectively and enhance ion diffusivity and electron conductivity. Gao et al. [76] applied free arc thermal excitation to disperse CNT agglomerations to fluffy CNT aerogels onto the surface of NiCo$_2$O$_4$ nanoneedles pre-formed on nickel foam. The loading amount of CNTs could be easily controlled by excitation time. CNTs and nanoneedles remained an intertwined morphology. A binder-free composite made of NiO$_2$-decorated CNTs and NiCo$_2$O$_4$ nanoparticles on nickel foam was prepared by electrophoretic deposition to form a stable electrode [77]. The highly conductive porous matrix of CNTs provided efficient electron transfer, high-surface area, and superior electrochemical performances.

In addition to nickel foam, stainless steel was also selected as a current collector. NiCo$_2$O$_4$/CNT electrodes were fabricated via an electrophoretic deposition on stainless steel plates from ethanolic suspension where Al(NO$_3$)$_3$ was used as the charging agent [78].
Compared with the pure NiCo$_2$O$_4$ electrode, the composite electrode exhibited a higher specific capacitance of 1540 F g$^{-1}$ at 3.5 A g$^{-1}$.

A 3D self-assembled carbon block matrix containing CNTs can be constructed by electrospinning, the replication method, and filtration. The conductive matrix can serve as a current collector. Then, after integrating with NiCo$_2$O$_4$, the hybrid can also be used as electrodes directly. El-Shafei et al. [79] reported the deposition of hierarchical NiCo$_2$O$_4$ nanostructures on the surface of the carbon nanofibers mat that was prepared by electrospinning polyacrylonitrile. The composite was applied as a free-standing electrode and showed a high-specific capacitance of 540 F g$^{-1}$ at 1 A g$^{-1}$. A 3D carbon sponge composed of single-walled CNTs/graphene was prepared by a dipping and burning method, and NiCo$_2$O$_4$ nanosheets were deposited on the carbon scaffolds by the hydrothermal method [80]. The hybrid could act as self-standing and binder-free electrodes and exhibited a high gravimetric capacitance of 2050 F g$^{-1}$ at 2 A g$^{-1}$. The porous structure served as robust ion reservoirs to buffer the volume changes during the Faradaic redox reactions. Yang et al. [81] prepared 3D block matrix composites of GO and CNTs by vacuum filtration. As shown in Figure 5a,b, such a structure had a layer-by-layer morphology with CNTs between the GO layers. In the hybrid, NiCo$_2$O$_4$ was deposited on the surface of the matrix through the hydrothermal process in Figure 5c,d. The hybrid electrode delivered a specific capacitance of 1525 F g$^{-1}$ at 1 A g$^{-1}$.

![Figure 5. SEM images of (a,b) GO/CNTs and (c,d) NiCo$_2$O$_4$@GO/CNTs at different magnifications. Reproduced with permission from [81]. Copyright 2019, Elsevier.](image)

### 4. Composites of NiCo$_2$O$_4$ and Amorphous Carbon

Because graphene and CNTs are graphitic crystalline carbon materials, both have high conductivities. Thus, the total resistance of the composites shows reduced values when being used as electrodes of supercapacitors. However, some amorphous carbon materials are also reported to integrate with NiCo$_2$O$_4$, though their conductivity is not very high. The mesoporous carbon/NiCo$_2$O$_4$ composite was prepared by co-precipitation and used for supercapacitors, as first reported by Qian et al. [82]. These carbon materials can be derived from biomass [83], polymers, and metal organic frameworks. The preparation methods for amorphous carbon materials include template synthesis, electrospinning, etc.
A variety of materials have been reported as templates to prepare porous carbon. Carbon-coated NiCo$_2$O$_4$ hollow microspheres were prepared using silica microspheres as templates, and the composite showed a specific capacitance of 637.5 F g$^{-1}$ at 0.5 A g$^{-1}$ [84]. NiCo$_2$O$_4$ nanorods decorated on 3D graphene-like amorphous carbon were prepared by a molten salt template method followed with a hydrothermal process where 3D porous carbon played a key role in reducing resistance and improving ion transport channels [85]. NaCl was used as a 3D aggregate template, and the composite had a specific capacitance of 1297 F g$^{-1}$ at 0.5 A g$^{-1}$. The 3D NiCo$_2$O$_4$ nanosheets-decorated, N-doped carbon nanocages were synthesized for supercapacitor electrodes by etching cubic Fe$_2$O$_3$ as the template. As demonstrated in Figure 6a,b, the product shows a cubic morphology with size about 0.8~1 µm. Figure 6c verifies the hierarchical hollow structure, and an HRTEM image in Figure 6d shows three lattice fringes from NiCo$_2$O$_4$ and carbon. Due to the synergistic effect of a hollow nanocage structure coupled with a built-in electric field, the hybrid could store energy up to 966.2 F g$^{-1}$ at 0.5 A g$^{-1}$ [86].

![Figure 6](image_url)

**Figure 6.** SEM (a,b), (c) TEM, and (d) HRTEM images of hollow N-doped carbon/NiCo$_2$O$_4$. Reproduced with permission from [86]. Copyright 2020, Elsevier.

Biomass materials have become promising for renewable supercapacitors. Biomass carbon-based porous microsheets were obtained by ultrasonically crushing the carbonized poplar catkins micro-hollow fibers. After modification by polydopamine and NiCo$_2$O$_4$ nanosheets in sequences, a sandwich composite was formed. It delivered a specific capacity of 922.9 C g$^{-1}$ at 1 A g$^{-1}$ [87]. However, biomass-derived carbon usually has the disadvantages of poor wettability and inferior areal capacitance. Nguyen et al. [88] synthesized composites of NiCo$_2$O$_4$ nanoparticles and mesoporous carbon using molten sugar as a carbon source, and it exhibited better electrochemical properties compared with carbon or pristine NiCo$_2$O$_4$. Zeng et al. [89] prepared porous graphene/wood-derived carbon aerogels to support NiCo$_2$O$_4$ by hydrothermal synthesis, and the composites exhibited a high-areal capacitance of 8.54 F cm$^{-2}$ at 1 mA cm$^{-2}$. The activation of ZnCl$_2$ could create more mass transport paths and increase wettability.
Metal organic framework (MOF)-derived metal oxide composites can be also applied to prepare stable composites of metal oxides and carbon. Thermal treatment of NiCo-MOFs could produce NiCo$_2$O$_4$ and amorphous carbon, which exhibited good electron and ion transport capability for Li-ion capacitors. [90]. Wang et al. [91] heated Ni-Co MOF pre-formed on a N-doped hollow carbon nanosphere to obtain NiCo$_2$O$_4$/carbon nanospheres. The hybrid showed a specific capacity of 166 mAh g$^{-1}$ at 1 A g$^{-1}$, as well as good cyclic stability. Recently, Zhou [92] prepared 3D flower-like NiCo$_2$O$_4$ derived from MOF materials that encapsulated by ultrathin N-doped carbon for supercapacitors, providing a close contact between the metal oxides and the carbon skeleton, as shown in Figure 7. In the elemental mappings in Figure 7, transition metals, C and N, are distributed uniformly in the composite. The 3D structured composite showed a specific capacitance of 1263 F g$^{-1}$ at 1 A g$^{-1}$.

Similar to MOFs, the electrospinning method can easily fabricate a 1D nanostructure with different elements in the polymeric matrix [93,94]. Xu et al. [95] prepared 1D carbon fibers incorporated with NiCo$_2$O$_4$ by electrospinning and heat treatment for supercapacitors where discrete NiCo$_2$O$_4$ nanoparticles embedded in an amorphous carbon matrix. As displayed in Figure 7a, the growth of discrete NiCo$_2$O$_4$ nanoparticles on carbon nanofibers is confirmed. The EDS mappings in Figure 7b show the homogeneity of elements in nanoscale. NiCo$_2$O$_4$ embedded N-doped carbon composite could be synthesized by the same method where polyvinylpyrrolidone was used as the carbon sources [96]. NiCo$_2$O$_4$ and N-doped carbon had enhanced electron mobility according to the calculated density of states. The hybrid delivered a specific capacitance of 2000.6 F g$^{-1}$ at 1A g$^{-1}$. Luo et al. [97] used polycrylonitrile to electrospin NiCo$_2$O$_4$ embedded carbon fibers for supercapacitors, exhibiting a specific capacitance of 836 F g$^{-1}$ at 5A g$^{-1}$.

![Figure 7.](image)

Different from the above cases, carbon nanofibers obtained by the electrospinning method are also reported as scaffold to prepare core-shell structured electrode materials. Sun et al. [98] prepared NiCo$_2$O$_4$ nanosheet-decorated carbon nanofibers by the hydrothermal route where NiCo$_2$O$_4$ nanosheets were uniformly grown on carbon nanofibers. The hybrid achieved a specific capacitance of 620 F g$^{-1}$ at 0.5 A g$^{-1}$ with good flexibility.
El-Deen et al. [99] deposited NiCo$_2$O$_4$ nanorods on the surface of carbon nanofibers that were obtained by carbonization of electrospun polyacrylonitrile at high temperatures. The hybrid achieved a specific capacitance of 649 F g$^{-1}$ at 3A g$^{-1}$, higher than the 260 F g$^{-1}$ for pristine NiCo$_2$O$_4$ and 66 F g$^{-1}$ for carbon nanofibers.

5. Summary and Prospects

Nickel cobaltite has been considered as a potential electrode material of supercapacitors for more than one decade. The combination of it with carbon materials can show much more robust electrochemical performances than carbon and pristine NiCo$_2$O$_4$, and the intrinsic disadvantages of NiCo$_2$O$_4$ can be overcome to a large extent.

Carbon materials typically having high crystallinity, and large-surface areas are very welcome to integrate with NiCo$_2$O$_4$ because the hybrid tends to display amplified conductivity and enlarged surface areas. Compared with 1D CNTs, 2D graphene is more widely investigated because of its high-surface areas, abundant functional groups on surfaces, and latest novelty, which can be easily identified from the volume of published papers. The composites of rGO and NiCo$_2$O$_4$ can present powder products, flexible films, and 3D aerogels. Some free-standing hybrid films can even serve as a binder-free electrode directly. However, the previous reports have confirmed that the mass ratio of NiCo$_2$O$_4$ to rGO is critical to the final electrochemical performances. Meanwhile, N-doping has been popularly reported to enhance the conductivity of rGO.

Though the reports on the hybrid of NiCo$_2$O$_4$/CNTs for supercapacitors are not a large amount, the hybrids have also displayed rather remarkable performances for supercapacitors. The surface treatment is generally required for the attachment of NiCo$_2$O$_4$. The hybrids of NiCo$_2$O$_4$ and CNTs anchored on current collectors commonly deliver a higher specific capacitance than powder composites. Some physical methods, such as electrophoretic deposition and arc thermal excitation, can disperse materials on substrates uniformly.

Amorphous carbon usually has high-specific surface areas and plentiful pores, as well as various architectures. Thus, it was also selected to combine with NiCo$_2$O$_4$ for high-performance electrodes. The template method and electrospraying are widely applied for the preparation of carbon materials where polymers and biomass are employed as carbon sources. Meanwhile, MOFs are suitable precursors to obtain a homogeneous mixture of NiCo$_2$O$_4$ and carbon that can exhibit a high ability to store energy.

In comparison to those amorphous carbon materials, the composites consisting of NiCo$_2$O$_4$ and graphene (or CNTs) can easily achieve a higher mass content of NiCo$_2$O$_4$ because of the nano-sized morphology. The contribution from EDLC is then negligible, and the chief role of carbon nanomaterials is building conductive pathways in the electrode. Thus, the composites will show more enhanced electrochemical performances. For the amorphous carbon derived from biomass and prepared by electrospraying, it is hard to realize a high loading of NiCo$_2$O$_4$ on carbon matrix.

Some effective strategy methods are suggested here to further improve the electrochemical performance of these kind of composites. Guest metal doping in NiCo$_2$O$_4$ can enhance its conductivity, and there are limited reports on this topic. A thin conductive interface film with good affinities to both NiCo$_2$O$_4$ and carbon can be introduced between them to achieve a close contact between them. Carbon materials with high crystallinity are welcome, owing to the high conductivity, but the surface treatment will lead to additional processing. Nitrogen doping on a carbon surface will change wettability and enhance conductivity. Compared with powder composites, binder-free hybrid films on current collectors demonstrate more robust properties.

Author Contributions: Conceptualization, J.X. and J.C.; writing—original draft preparation, J.X. and Y.S.; writing—review and editing, J.C. and X.W.; visualization, Y.S.; funding acquisition, J.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science Foundation of Zhejiang Province (No. LY18E020003).
Conflicts of Interest: The authors declare no conflict of interest.

References


42. Chao, Y.; Feng, G.; Wang, W.; Zhang, X.; Cao, Y. Facile synthesis of fluorinated graphene/NiCoO₂ nanorods composite with high supercapacitive performance. *Appl. Nanosci.* 2022, 12, 1–8. [CrossRef]


