



Review

NiCo₂O₄-Based Supercapacitor Nanomaterials

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Abstract: In recent years, the research on supercapacitors has ushered in an explosive growth, which mainly focuses on seeking nano-/micro-materials with high energy and power densities. Herein, this review will be arranged from three aspects. We will summarize the controllable architectures of spinel NiCo₂O₄ fabricated by various approaches. Then, we introduce their performances as supercapacitors due to their excellent electrochemical performance, including superior electronic conductivity and electrochemical activity, together with the low cost and environmental friendliness. Finally, the review will be concluded with the perspectives on the future development of spinel NiCo₂O₄ utilized as the supercapacitor electrodes.

Keywords: supercapacitors; spinel NiCo₂O₄; nano-/micro-materials

1. Introduction

Over the past few decades, the rapid development of the global economy has increased the demands of energy, and the ever-urgent demands to seek other renewable and environmentally-friendly energy sources to reduce the dependence on fossil fuels prompted the developments of storage and conversion technologies [1,2]. However, the renewable energy sources have intermittent features for their access, which can be easily influenced by external conditions. Though the technologies of harvesting renewable energy, such as fuel cells, lithium-ion batteries and dye-sensitized solar cells, and so on [3–5], have been remarkably improved, further appropriate technologies to capture and store the generated energy are still required. In recent years, supercapacitors, the new devices between conventional physical capacitors and batteries, also known as electrochemical capacitors, have been extensively studied to serve as one of the most promising candidates for next-generation energy storage devices due to their intriguing properties, such as high power densities, long cycling lifespans and fast charge/discharge processes, which can be proven by the number of literature works shown in Figure 1.

Generally, supercapacitors can be divided into two types, electrical double-layer capacitors (EDLCs) and pseudocapacitors (PCs), including three major categories of materials: carbonaceous materials, conducting polymers and transition metal oxides/hydroxides (TMO/Hs), depending on their different charge storage mechanisms [6,7]. The EDLCs are based on the electrical double-layer theory, which was put forward by German physicist Helmholtz in 1874 [8], and subsequently revised by Gouy, Stern, etc. [9,10]. In 1957, the practical application of a double-layer capacitor to store electrical charge was demonstrated and patented by H.I. Becker [11]. As shown in Figure 2a, the energy storage

of EDLCs occurs at the interfaces between the electrodes' active materials and electrolytes, which is a pure physical charge accumulation at the interfaces [12]. The EDLCs can be simplified to be the parallel-plate capacitors with the formula as follows [13,14]:

$$C = \frac{\epsilon_0 \epsilon_r}{d} A \quad (1)$$

where ϵ_r refers to the dielectric constant of electrolyte, ϵ_0 represents the permittivity of a vacuum, d is the Debye length and A is the effective area, which contacts electrolyte. The formula obviously shows that the C is greatly influenced by the specific surfaces. Carbonaceous materials, which possess high specific surfaces, good electrical conductivity, high chemical stability, low cost, etc., have been widely utilized for EDLCs. However, carbonaceous materials still suffer from limited specific capacitances and lower energy density, which restrict their large-scale commercialization [15]. On the contrary, pseudocapacitance was first investigated by Conway in the 1960s, and the PCs mainly depend on fast reversible faradic redox reactions on the surface [16–18], which is schematically illustrated in Figure 2b. Conducting polymers, TMO/Hs, carbonaceous materials enriched in heteroatoms (oxygen, nitrogen) and nanoporous carbons with electro-absorbed hydrogen can be classified into pseudocapacitive materials [19–21].

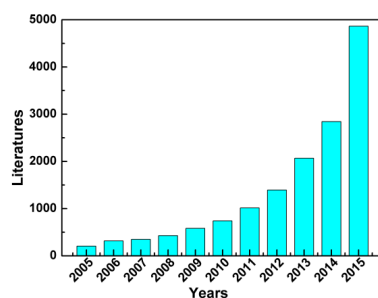


Figure 1. The numbers of reported literature works related to supercapacitors from 2005 to 2015 (search from the Web of Science with “supercapacitor” as the keyword).

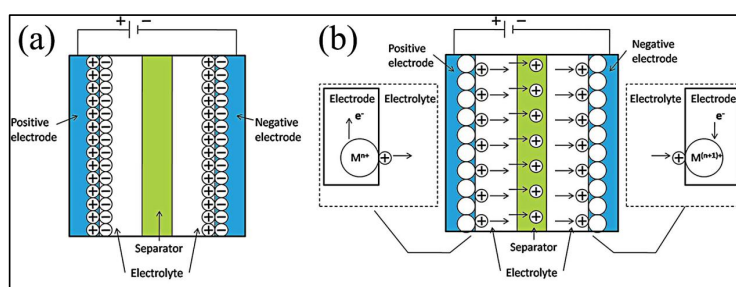


Figure 2. Schematic illustration of different types of supercapacitors: (a) electrical double-layer capacitors (EDLCs); (b) pseudocapacitor (PCs) (M represents the metal atom; if anions in the electrolyte take part in the reversible redox reaction, they will move in the opposite direction to the cations) (Reproduced with permission from [22]. Copyright the Royal Society of Chemistry, 2014).

Additionally, the performance of a supercapacitor is greatly influenced by a series of significant fundamental parameters. Energy density and power density possess great significance on evaluating the performance of supercapacitors, which are mostly accessible for practical application and are usually significant to evaluate the supercapacitor devices. The energy density and power density can be calculated from the equations as follows [23–25]:

$$E = \frac{\int Iv(t)dt}{m} = \frac{1}{2 \times 3600} C_m V^2 \quad (2)$$

$$P = \frac{V^2}{4mR_s} = \frac{E}{\Delta t} \quad (3)$$

where E (Wh/kg) refers to the energy density, I (A) is the discharge current of the discharge process, $v(t)$ is the cell voltage, dt is a time differential, m is the total mass of the whole cell, C_m is gravimetrically-specific capacitance, V is the potential window, P (W/kg) is the power density, Δt is the discharging time and R_s refers to the equivalent series resistance (ESR). The equations show that the specific capacitance, potential window and ESR have great influence on the energy density and power density. In addition, Ragone plots displaying energy density versus power density are shown in Figure 3, which points out that the supercapacitors are new devices and have filled the gap between batteries and conventional dielectric capacitors with higher energy density than conventional dielectric capacitors and larger power density than batteries [26]. Therefore, considerable interest has been focused on hunting for high-performance electrode materials with higher capacitance, a wider potential window and lower resistance to improve the energy and power density of electrode materials. TMO/Hs have become the representative pseudocapacitor materials because they have multiple valences for charge transfer and reversible adsorption properties, resulting in higher specific capacitance and larger energy density, such as Ru-based, Mn-based, Ni-based, etc., materials [27–29]. Among them, RuO_2 delivered superior electrochemical performance, including high specific capacitance, energy density and power density on account of its favorable conductivity and highly reversible redox process [30]. However, its high toxicity, high costs and being a scarce resource extremely restrict the convenience of application at a large scale. Therefore, it seems very useful to seek materials with excellent properties containing environmentally-friendly and favorable electrochemical performance.

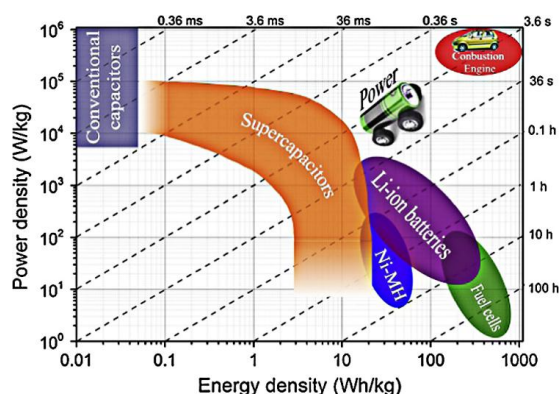


Figure 3. Ragone plots for various electrochemical energy storage systems (Reproduced with permission from [26]. Copyright Elsevier, 2015).

Spinel NiCo_2O_4 , as one of the most promising candidates of typical TMO/Hs, has attracted great attention, not only possessing low cost, being an abundant resource and being environmentally benign compared with Ru-based materials, but also have better electrical conductivity and higher electrochemical activity than Mn-based and V-based materials [24,25]. Although spinel NiCo_2O_4 has received considerable research interest due to its series of excellent features, there are few reviews to summarize the most important related work and achievements of NiCo_2O_4 -based materials on the application of supercapacitors. Therefore, we will summarize the syntheses (including various fabrication methods, different architectures) and performance of NiCo_2O_4 materials as supercapacitor electrodes.

2. Synthetic Strategies and Performance for NiCo_2O_4 -Based Nanomaterials

Generally, binary metal oxides NiCo_2O_4 have a cubic spinel structure (as depicted in Figure 4a), where nickel ions occupy the octahedral sites, and cobalt ions spread on both the octahedral and

tetrahedral sites [31–33]. Furthermore, the abundant resources and low toxicity of nickel and cobalt materials signify low cost and environmental friendliness. The electronic conductivity and electrochemical activity of spinel NiCo_2O_4 as shown in Figure 4b are superior to those of nickel oxides and cobalt oxides by at least two orders of magnitude [34,35], which can greatly influence the supercapacitive performances, especially on the power density. What is more, the supercapacitive performances of NiCo_2O_4 -based materials are dominated by the richer faradic redox reactions in alkaline electrolytes originated from both nickel and cobalt ions [33,36]. The redox reactions in alkaline electrolytes can be ascribed as follows [37–39]:

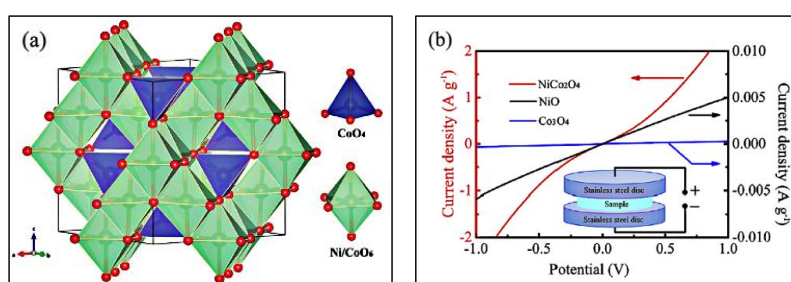
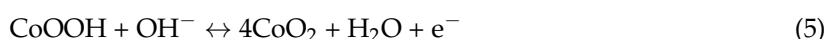
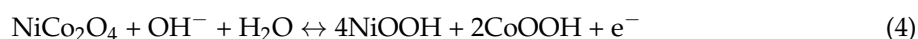


Figure 4. (a) Crystallographic structure of the spinel NiCo_2O_4 unit cell (Reproduced with permission from [35]. Copyright the Royal Society of Chemistry, 2015); (b) I - V curves of the as-synthesized NiCo_2O_4 , NiO and Co_3O_4 samples (Reproduced with permission from [34]. Copyright Elsevier, 2015).

2.1. Approaches to Synthesize NiCo_2O_4 Nanomaterials

To date, many methods have been reported to synthesize and improve the performance of spinel NiCo_2O_4 , such as hydrothermal, sol-gel, electrochemical deposition, etc. Different architectures of spinel NiCo_2O_4 are obtained as shown in Table 1. It is worth mentioning that all of these methods tend to synthesize the precursor of NiCo_2O_4 firstly, and a calcination procedure followed to get the spinel NiCo_2O_4 is needed. Therefore, in this section, we will describe the most widely-applied procedures to synthesize spinel NiCo_2O_4 materials and their products.

2.1.1. Hydrothermal/Solvothermal Method

The hydrothermal/solvothermal method has received much attention, mainly due to its simplicity, low cost, high efficiency and convenient manipulation combined with flexible control over the sizes and morphologies of the resulting nanostructures, in which aqueous or other solvents are used as the reaction mediums to generate a high temperature and high pressure reaction environment by heating the reaction vessel to a certain temperature [40,41]. Therefore, this method is extensively used to form the precursors of NiCo_2O_4 nanomaterials by heating the homogeneous solution of nickel and cobalt salts and other surfactant agents or structure-controlled agents in a sealed Teflon-lined stainless steel autoclave. The possible reactions in the hydrothermal process are as described by the following equations [38,42]:

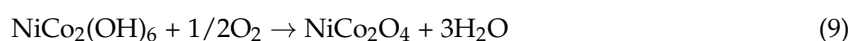
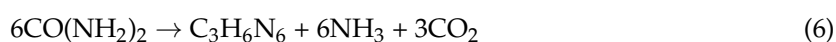


Table 1. Pure NiCo₂O₄ nanostructures.

| Material | Preparation Methods //Annealing Condition | Specific Capacitance //Loading Mass | Rate Performance | Capacity Retention | Potential Window//Electrolyte | Ref. |
|---|--|---|--|--|--|------|
| urchin-like NiCo ₂ O ₄ | hydrothermal 120 °C/6 h //300 °C/3 h in air | 1650 F/g (at 1 A/g) | 1348 F/g (at 15 A/g) | 90.8% (after 2000 cycles) | 0–0.41 V vs. SCE// 3 M KOH | [33] |
| flowerlike NiCo ₂ O ₄ | hydrothermal 180 °C/6 h //300 °C/2 h in air | 658 F/g (at 1 A/g) | 78% (at 20 A/g) | 93.5% (after 10,000 cycles) | 0–0.55 V vs. Hg/HgO// 6 M KOH | [34] |
| NiCo ₂ O ₄ nanosheets | electrodeposition (–1.0 V vs. SCE) //300 °C/2 h | 2010 F/g (at 2 A/g) //0.8 mg/cm ² | 72% (at 20 A/g) | 94% (after 2400 cycles) | –0.1–0.3 V vs. SCE// 3 M KOH | [37] |
| NiCo ₂ O ₄ double-shell hollow spheres | hydrothermal 90 °C/4 h //300 °C/4 h | 718 F/g (at 1 A/g) //3.76 mg/cm ² | 80% (at 10 A/g) | 89.9% (after 2000 cycles) | 0–0.4 V vs. SCE// 6 M KOH | [38] |
| flower-like nickel-cobalt Oxides | hydrothermal 120 °C/2h //300 °C/2h | 750F/g (at 1A/g) 2.2mg/cm2 | 498F/g (at 10 A/g) | 102% (after 3000 cycles) | 0-0.5V vs. Ag/AgCl// 2M KOH | [39] |
| NiCo ₂ O ₄ nanowires | hydrothermal 100 °C //300 °C/3 h | 1283 F/g (at 1 A/g) //1.2 mg/cm ² | 79% (at 20 A/g) | 100% (after 5000 cycles) | 0–0.4 V vs. SCE// 6 M KOH | [42] |
| NiCo ₂ O ₄ nanorods/nanosheets | oil bath 80 °C/6 h //300 °C/2 h 90 °C/4 h //350 °C/2 h | nanorods 1023.6 F/g (at 1 A/g) nanosheets 1002 F/g (at 1 A/g) | 500 F/g (at 20 A/g) 520 F/g (at 20 A/g) | 81.5% (after 2000 cycles) 96.4% (after 2400 cycles) | 0–0.45 V (nanorods) 0–0.55 V (nanosheets) vs. SCE// 2 M KOH | [43] |
| chain-like NiCo ₂ O ₄ nanowires | hydrothermal 100 °C/6 h //300 °C/2 h in air | 1284 F/g (at 2 A/g) | 72% (at 20 A/g) | 97.5% (3000 cycles) | 0–0.43 V vs. Ag/AgCl// 6 M KOH | [44] |
| NiCo ₂ O ₄ spinel thin-film | potentiostatic deposition //200 °C | 580 F/g (at 0.5 A/g) | 570 F/g (at 50 A/g) | 94% (after 2000 cycles) | 0.1–0.45 V vs. Ag/AgCl// 1 M KOH | [45] |
| NiCo ₂ O ₄ NSs@hollow microrod arrays | electrochemical deposition //300 °C/2 h | 678 F/g (at 6 A/g) | 367 F/g (at 47 A/g) | 96.06% (after 1500 cycles) | 0-0.5 V vs. SCE// 1 M KOH | [46] |
| NiCo ₂ O ₄ nanosheet | electrochemical deposition //300 °C/2 h in air | 2658 F/g (at 2 A g ^{–1}) //0.6 mg/cm ² | 70% (at 20 A g ^{–1}) | 80% (after 3000 cycles) | –0.1–0.35 V vs. Hg/Hg ₂ Cl ₂ // 3 M KOH | [47] |
| NiCo ₂ O ₄ nanotubes | electrospun //450 °C/2 h in air | 1647 F/g (at 1 A/g) | 77.3% (at 25 A/g) | 93.6% (after 3000 cycles) | 0–0.41 V vs. Ag/AgCl// 2 M KOH | [48] |

Table 1. Cont.

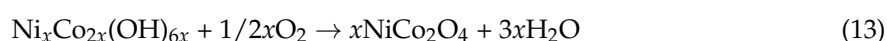
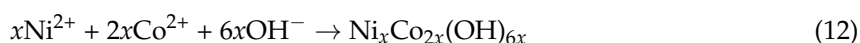
| Material | Preparation Methods //Annealing Condition | Specific Capacitance //Loading Mass | Rate Performance | Capacity Retention | Potential Window//Electrolyte | Ref. |
|--|--|---|---|--|---------------------------------------|------|
| NiCo ₂ O ₄ nanosheets | hydrothermal 90 °C/10 h //320 °C/2 h in air | 3.51 F/cm ² (at 1.8 mA/cm ²) //1.2 mg/cm ² | 39% (at 48.6 mA/cm ²) | 93.3% (8.5 mA/cm ²) 82.9% (25 mA/cm ²) (after 3000 cycles) | 0–0.45 V vs. SCE// 2 M KOH | [49] |
| NiCo ₂ O ₄ nanosheets | oil bath 90 °C/6 h //300 °C/2 h | 899 F/g (at 1 A/g) //1.54 mg/cm ² | 67.9% (at 20 A/g) | 93.2% (6000 cycles//2 A/g) 84.9% (6000 cycles//5 A/g) | 0–0.45 V vs. SCE// 6 M KOH | [50] |
| NiCo ₂ O ₄ nanosheets @halloysite nanotubes | oil bath 90 °C/6 h //350 °C/3.5 h in air | 1886.6 F/g (at 6 A/g) | 79.5% (at 30 A/g) | 94.74% (after 6000 cycles) | 0–0.5 V vs. SCE// 2 M KOH | [51] |
| NiCo ₂ O ₄ nanowires | precipitate //250 °C/3 h | 743 F/g (at 1 A/g) | 78.6% (at 40 A/g) | 93.8% (after 3000 cycles) | –0.05–0.45 V vs. Ag/AgCl// 1 M KOH | [52] |
| NiCo ₂ O ₄ spheres | oil bath 180 °C/3 h //300 °C/3 h | 856 F/g (at 1 A/g) | 60.8% (at 100 A/g) | 98.75% (after 10,000 cycles) | 0–0.5 V vs. Hg/HgO// 2 M KOH | [53] |
| flower-shaped NiCo ₂ O ₄ microsphere | microwave-assisted 100 °C/15 min //300 °C/2 h in air | 1006 F/g (at 1 A/g) //3 mg/cm ² | 72.2% (at 20 A/g) | 93.2% (after 1000 cycles) | 0–0.5 V vs. Hg/HgO// 6 M KOH | [54] |
| NiCo ₂ O ₄ nanoneedle | hydrothermal 85 °C/8 h //250 °C/1.5 h | 3.12 F/cm ² (at 1.11 mA/cm ²) //0.9 mg/cm ² | 18.9% (at 22.24 mA/cm ²) | 94.74% (after 2000 cycles) | 0–0.4 V vs. SCE// 2 M KOH | [55] |
| NiCo ₂ O ₄ multiple hierarchical structures | hydrothermal 120 °C/7 h //350 °C/3 h | 2623.3 F/g (at 1 A/g) //2.09 mg/cm ² | 1785.5 F/g (at 40 A/g) | 94% (after 3000 cycles) | 0–0.5 V vs. Hg/HgO// 3 M KOH | [56] |
| Nickel cobaltite nanowire | hydrothermal 150 °C/6 h //350 °C/3 h in air | 760 F/g (at 1 A/g) //1 mg/cm ² | 70% (at 20 A/g) | 81% (after 3000 cycles) | –0.05–0.50 vs. Hg/HgO// 6 M KOH | [57] |
| NiCo ₂ O ₄ nanowire | hydrothermal 120 °C /6 h //400 °C/3 h | 2681 F/g (at 2 A/g) //3 mg/cm ² | 2305 F/g (at 8 A/g) | 100% (after 3000 cycles) | 0–0.45 V vs. SCE// 3 M KOH | [58] |
| NiCo ₂ O ₄ square sheet | hydrothermal 180 °C/24 h //350 °C/3 h | 980 F/g (at 0.5 A/g) | 384 F/g (at 10 A/g) | 91% (after 1000 cycles) | 0–0.5 V vs. Ag/AgCl// 1 M KOH | [59] |
| NiCo ₂ O ₄ nanosheets | microwave 140 °C/30 min //300 °C/3 h in air | 560 F/g (at 2 A/g)// 1 mg/cm ² | 71% (at 20 A/g) | 95.2% (after 5000 cycles) | 0–0.6 V vs. SCE// 2 M KOH | [60] |

The above-mentioned equations are more suitable for a temperature of no higher than 100 °C, and the precursors of $(\text{Co, Ni})_2\text{CO}_3(\text{OH})_2 \cdot n\text{H}_2\text{O}$ are obtained when the temperature is higher than 100 °C [54]. In addition, the intermediate products are also influenced by the surfactant agent and the organic solvent. However, whatever the procedure of the reactions, all of the end products of the hydrothermal/solvothermal method need to be appropriately annealed to obtain NiCo_2O_4 .

By the hydrothermal/solvothermal method, the morphologies can be easily adjusted by temperature, reactions times and reactions substances or other reactions conditions, in order to advance the supercapacitive performance of NiCo_2O_4 electrodes. For instance, Zou et al. [44] have fabricate 3D radial chain-like nanowire NiCo_2O_4 micro-spheres with different exposed crystal planes by a hydrothermal method. When applied as electrode materials for supercapacitors, chain-like NiCo_2O_4 nanowires exhibited high specific capacitance of 1284 F/g at 2 A/g, favorable rate capability and excellent cycling stability with only 2.5% loss after 3000 cycles. The results of in situ electrical properties clearly illustrated that the chain-like nanowires with different exposed crystal planes exhibit superior electronic conductivity, demonstrating that the electronic conductivity was very essential for electrode materials in supercapacitors. Moreover, Padmanathan et al. [61] have investigated the morphology conversions of bimetallic NiCo_2O_4 nanostructures on carbon fiber cloth (CFC) with different precursor salts in an equal volume of ethanol and water mixed solvent at 120 °C for 8 h, and they successfully prepared NiCo_2O_4 nanowall networks and porous nanoflake microstructures. The as-prepared NiCo_2O_4 nanowall network structures deliver a maximum capacitance of 1225 F/g at a high current density of 5 A/g; even at 40 A/g, the specific capacitance still remains 996 F/g, higher than the NiCo_2O_4 nanoflakes with only 844 F/g at 1 A/g. As a result, the surface morphology was successfully induced by the variation of the precursor, which proved the influence of the precursor on the growth kinetics and structure-property relations. Shen et al. [62] have reported the synthesis of uniform NiCo_2O_4 hollow spheres with a one-step hydrothermal method in the mixed organic solvent of 8 mL glycerol and 40 mL isopropanol, which exhibit excellent electrochemical properties with the favorable capacitance of 1141 F/g at 1 A/g and good cycling properties of only 5.3% loss after 4000 cycles. All of these reports demonstrate that the morphologies of the NiCo_2O_4 can be simply controlled by hydrothermal conditions and are accessible to pursue higher supercapacitive performances by adjusting the morphologies and architectures.

2.1.2. Electrochemical Deposition Method

The electrochemical deposition method is also widely employed for preparing NiCo_2O_4 by a three-electrode construction, in which the samples are precipitated and deposited on the conductive substrates in an as-prepared homogeneous solution of nickel and cobalt salts. NiCo_2O_4 nanoarchitectures are obtained by the post-annealed process. The procedure of these electrochemical reactions and the sequences are as described by the following equations [63–65]:



where NO_3^- was reduced on the cathodic surface and simultaneously generated OH^- ions. Subsequently, the generation of OH^- ions at the cathode combines the Ni^{2+} or Co^{2+} to form uniform precipitation of $\text{Ni}(\text{OH})_2$ or $\text{Co}(\text{OH})_2$ nanomaterials. Moreover, the solubility constant (K_{sp}) of $\text{Co}(\text{OH})_2$ (2.5×10^{-16}) is very close to $\text{Ni}(\text{OH})_2$ (2.8×10^{-16}) at 25 °C, which means that the composition of the product can be controlled by adjusted the molar ratio of Ni^{2+} and Co^{2+} . On account of the homogeneous morphology of production, high efficiency and convenient manipulation, electrochemical deposition

has been widely used as the technique to synthesize electrode materials with a stably-uniform morphology, which possess ultrahigh specific capacitances and favorable cycling performances.

As early as 2010, Gupta et al. [45] successfully prepared spinel NiCo_2O_4 thin-film on stainless-steel by using a three-electrode electrochemical configuration in a mixed electrolyte of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.55:0.45 in molar ratio) at -1.0 V (vs. Ag/AgCl). Then, to optimize the performance, they investigated the influence of difference annealing temperatures and found that the morphology of the as-prepared NiCo_2O_4 thin-film was greatly affected by the temperature. When annealed at 200 °C, the NiCo_2O_4 thin-film possesses a porous nanostructure with long-range interconnectivity promoting electrochemical accessibility of OH^- ion electrolyte and a high diffusion rate through the bulk, corresponding well to the results of high specific capacitance, good rate capability and cycling performance. Additionally, Yuan et al. [37] synthesized ultrathin mesoporous (with a size range from 2 to 5 nm) nickel cobaltite (NiCo_2O_4) nanosheets on conductive nickel foam by involving co-electrodeposition (electrodeposition potential is -1.0 V vs. SCE) of a bimetallic (Ni, Co) hydroxide precursor onto a Ni foam and followed thermal transformation to spinel mesoporous NiCo_2O_4 . These structures promise fast electron and ion transport, a large electroactive surface area, and excellent structural stability, exhibiting ultrahigh specific capacitance of 2010 F/g at the current densities of 2 A/g and still remaining at 1450 F/g even at a very high current density of 20 A/g. In addition to the potentiostatic deposition, Wu and his coworkers [35] have prepared homogeneously thin NiCo_2O_4 nanosheets on the skeleton of 3D Ni foam/N-CNT by using constant cathodic current under 1 mA/cm² for 10 min at room temperature. The 3D Ni foam/N-CNT/ NiCo_2O_4 nanosheet electrode exhibits superior supercapacitive performances with high specific capacitance (1472 F/g at 1 A/g), a remarkable rate capability and excellent cycling stability (less than 1% loss after 3000 cycles). Recently, Zeng et al. [66] synthesized NiCo_2O_4 nanosheets by cyclic voltammetry (CV) conducted in a potential range of -1.1 V– -0.5 V with a sweep rate of 20 mV/s for 20 cycles. The high areal capacitance (3.18 F/cm² at 6 mA/cm²) (2650 F/g at 5 A/g), good rate capability and cycling stability (76% capacitance retention after 4000 cycles at a high current density of 10 mA/cm²) reveal the feasibility of these methods and these smart structures. These different approaches of electrochemical deposition demonstrate that the synthesized conditions of NiCo_2O_4 nanosheets are very flexible. Owing to these many advantages of electrochemically-deposited NiCo_2O_4 nanomaterials, there are many advanced electrodes, such as NiCo_2O_4 nanosheet@hollow microrod arrays [46], 3D interconnected mesoporous NiCo_2O_4 @ $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ core-shell nanosheet arrays [67], three-dimensional nickel foam/graphene/ NiCo_2O_4 [68], hybrid composite $\text{Ni}(\text{OH})_2$ @ NiCo_2O_4 [69] and hierarchical Co_3O_4 @ NiCo_2O_4 nanowire arrays [70].

2.1.3. Other Methods

The hydrothermal/solvothermal method and electrochemical deposition method are the two common approaches to synthesize NiCo_2O_4 -based nanomaterials for supercapacitor electrodes. It is obvious that the hydrothermal/solvothermal method tends to control the size and nanostructure by adjusting the reagents or concentration and reaction time or temperature to optimize the performance. By contrast, all of the morphologies of the electrochemical deposition method are inclined toward the structures of nanosheets. Nevertheless, the merits of the electrochemical deposition method are quite apparent. These ultrathin nanosheets not only enlarge the specific surface area and increase the electroactivity, but also retained much interparticle porosity and interspace to facilitate the diffusion of the electrolyte. Furthermore, it is easy to deposit the NiCo_2O_4 nanosheets on conductive substrates or other superior performance materials by the electrochemical deposition method, which can further stimulate the performance.

However, in addition to the hydrothermal/solvothermal method and electrochemical deposition method, there are other ways to prepare spinel NiCo_2O_4 nanomaterials for supercapacitor electrodes, further demonstrating the advantages of the facile preparation. For instance, Wei et al. [36] first obtained NiCo_2O_4 aerogels via an epoxide-driven sol-gel process in 2010, for which the specific

capacitance can be reached as 1400 F/g under a mass loading of 0.4 mg/cm² at a sweep rate of 25 mV/s within a potential window of 0.04 V–0.52 V in a 1 M NaOH solution. Li and co-workers [46] synthesized novel porous NiCo₂O₄ nanotubes by a single-spinneret electrospinning technique followed by calcination in air. The electrodes assembled by as-prepared NiCo₂O₄ nanotubes exhibited excellent properties, for which the specific capacitance reached 1647 F/g at 1 A/g; the rate capability maintained at 77.3% at 25 A/g; and the cycling stability exhibited only a 6.4% loss after 3000 cycles. Luo et al. [71] reported porous NiCo₂O₄-rGO by electro-spray, and Ding et al. [72] successfully synthesized mesoporous NiCo₂O₄ nanoparticles via a facile and cost-effective ball milling solid-state method, followed by a thermal treatment. Besides these approaches mentioned above, there are still other methods, such as microwave-assisted methods [54,73,74], co-precipitation methods [75,76], chemical bath deposition [77] and oil bath [43,51,78,79].

2.2. The Morphologies of NiCo₂O₄ Nanostructures

In order to improve the supercapacitive performances of NiCo₂O₄-based materials and broaden their applications, many researchers have dedicated their efforts to modify the structures and morphologies to further trigger the performance of NiCo₂O₄-based materials. Herein, we will summarize the morphologies of NiCo₂O₄ nanostructures and their performance.

2.2.1. 1D NiCo₂O₄ Nanostructures

1D nanostructures are usually categorized as those with a large aspect ratio (defined as the length along the longitudinal axis to the width along the transversal plane) [80], such as nanorods, nanowires, nanobelts and nanotubes. Among these various morphologies, 1D NiCo₂O₄ nanostructures are very common nanostructures, which is mainly due to their superior properties. The 1D NiCo₂O₄ nanostructures possess monodispersity, which ensures every nanowire participates in the electrochemical reaction relying on the favorable conductivity. Furthermore, the 1D NiCo₂O₄ nanostructures were formed by many smaller units retaining a large amount of pores, which facilitate the ion diffusion. What is more, the 1D NiCo₂O₄ nanostructures have excellent structure stability, meaning superior cycling performance. Wang et al. [57] synthesized NiCo₂O₄ nanowires by a facile hydrothermal method, followed by an annealing treatment. SEM and TEM images in Figure 5a show that the nanowires have a high aspect ratio with lengths up to several micrometers and diameters down to about 20 nm. What is more, the specific capacitance of these NiCo₂O₄ nanowires can reach as high as 760 F/g at the current density of 1 A/g, and retain 532 F/g at 20 A/g (about 70%, compared to the specific capacitance at 1 A/g). The specific capacitance is about 81% of the initial value after 3000 cycles, which indicates that the NiCo₂O₄ nanowires have high specific capacitance and remarkable rate capability. Jiang et al. [52] reported hierarchical porous NiCo₂O₄ nanowires by stirring the mixture and collecting the precipitates, and a calcination process was subsequently followed. From the SEM and TEM images (Figure 5b), the porous NiCo₂O₄ hierarchical nanowires are observed. These porous NiCo₂O₄ nanowires show a high specific capacitance of 743 F/g at 1 A/g with excellent rate performance (78.6% capacity retention at 40 A/g) and superior cycling stability (only 6.2% loss after 3000 cycles). Recently, Lou's group [81] reported hierarchical tetragonal microtubes consisting of ultrathin mesoporous NiCo₂O₄ nanosheets by a one-step solvothermal method. Additionally, these advanced structures endow the NiCo₂O₄ with intriguing performance, showing a high specific capacitance of 1387.9 F/g at the current density of 2 A/g, and 62% of the capacitance is still retained when the charge-discharge current density is increased from 2–30 A/g with the capacitance loss being only about 10.6% after 12,000 cycles. In addition, in order to analyze the mechanism of the formation, they further investigated the time dependency. Figure 5c reveals the evolution process of the Ni-Co precursors, where the smooth tetragonal nanoprisms with a pyramid-like apex at the end are obtained at the initial stage of the solvothermal reaction and evolved into completely hollow microtubes consisting of nanosheets.

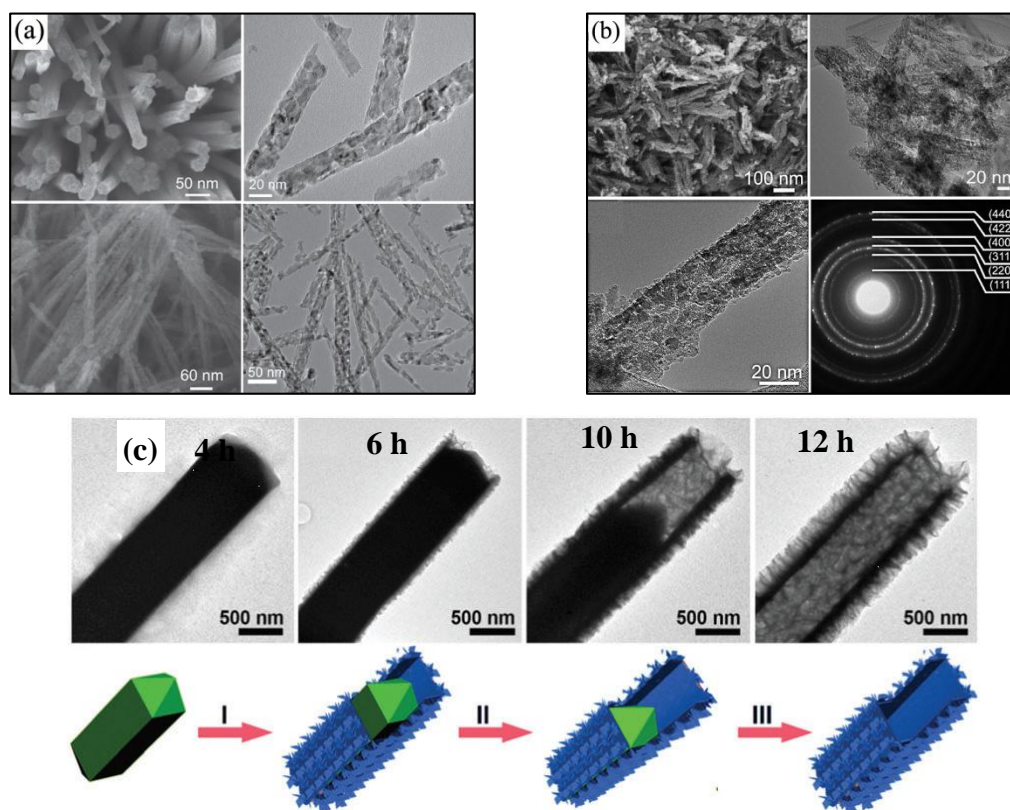


Figure 5. (a) Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of NiCo₂O₄ nanowires (Reproduced with permission from [57]. Copyright John Wiley and Sons, 2011); (b) SEM, TEM and selected area electron diffraction (SAED) of the porous NiCo₂O₄ nanowires (Reproduced with permission from [52]. Copyright the Royal Society of Chemistry, 2012); (c) TEM images of different reaction time and the schematic illustration of the formation process for hierarchical nickel cobalt layered double hydroxide tetragonal microtubes (Reproduced with permission from [52]. Copyright the Royal Society of Chemistry, 2012).

Although significant achievements have been made for 1D NiCo₂O₄ nanostructures, there is still big room for NiCo₂O₄ nanomaterials as supercapacitors to improve the performance. In the traditional method, the samples are mixed into a slurry and pasted to the current collector, which will suffer from inhomogeneity and limits the diffusion of electrolytes. Therefore, it will be of great significance to directly grow the NiCo₂O₄ nanostructures on conductive substrates. Shen and co-workers [42] directly grew NiCo₂O₄ nanowire arrays on carbon textiles, which displayed good dispersity (Figure 6a) and excellent supercapacitive performance. The distinctive electrode architectures enhanced the conductivity, and the large open spaces between neighboring nanowires would ensure every nanowire participated in the ultrafast electrochemical reaction, which greatly contributed to the electrochemical performance. The specific capacitance of NiCo₂O₄ nanowires arrays on carbon textiles was 1283 F/g at 1 A/g, and about 79% was retained even at 20 A/g, revealing the superior specific capacitance and rate capability. What is more, these porous NiCo₂O₄ nanowires exhibited remarkable cyclic stability with negligible specific capacitance decay after 5000 cycles, demonstrating its robust and superior performance as supercapacitor electrodes. Actually, the excellent electrochemical performance for the unique binder-free NiCo₂O₄/carbon textiles benefited from the intrinsic materials' and architectures' features. Moreover, Wang et al. [58] reported directly-grown NiCo₂O₄ nanowires on a conductive nickel foam substrate by a hydrothermal method (Figure 6b), whose specific capacitance can reach 2681 F/g at 2 A/g and 2305 F/g at 8 A/g. These results demonstrate that the substrates have great influence of the electrochemical performance, which is consistent with our previous work [41].

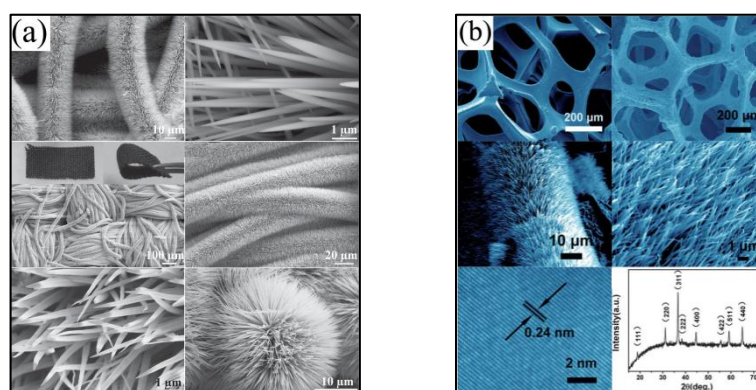


Figure 6. (a) Different magnification SEM images of NiCo₂O₄ nanowires arrays on carbon textiles (Reproduced with permission from [42]. Copyright John Wiley and Sons, 2014); (b) SEM image of the Ni foam and NiCo₂O₄ nanowires on Ni foam (Reproduced with permission from [58]. Copyright the Royal Society of Chemistry, 2013).

2.2.2. 2D NiCo₂O₄ Nanostructures

2D NiCo₂O₄ nanostructures, such as nanosheets, nanoplates and nanofilms, are other important architectures with superior supercapacitive performance as electrode materials. These 2D NiCo₂O₄ nanostructures greatly enlarge the specific surface area and electroactivity. Furthermore, the interconnected nanosheets retained massive interspaces, which facilitate the ion diffusion. What is more, these ultrathin nanosheets tend to combine other intriguing materials to form high dimensional nanostructures, which not only further improve the performance, but also increase the utilization of the space. As early as 2010, Gupta et al. [45] synthesized high-performance spinel NiCo₂O₄ nanosheets on stainless-steel with potentiostatic deposition by using an aqueous mixed electrolyte in a three-electrode electrochemical configuration. From the SEM images (Figure 7a), the average thickness of the obtained nanosheets was about 10 nm. Their specific capacitances reached 580 F/g at 0.5 A/g, and only a 6% decrease of the initial value was observed after 2000 cycles. Moreover, Lou's group reported many substantial methods to synthesize NiCo₂O₄ nanosheets that exhibited excellent performance, such as hydrothermal (Figure 7b) [49], oil bath [43,50] and electrodeposition method [37], which made tremendous contributions to the 2D NiCo₂O₄ nanostructures. Recently, Du and co-workers fabricated NiCo₂O₄ nanosheets by a three-electrode electrochemical configuration [47], in which the specific capacitance was as high as 2658 F/g at 2 A/g and still retained 1866 F/g at 20 A/g, and the specific capacitance reduced approximately 20% after 3000 cycles. Additionally, Garg et al. [59] prepared NiCo₂O₄ square sheets and hexagonal sheets by tuning the hydrolyzing agents in the hydrothermal method; these nanosheets showed excellent performance, especially for the square sheets. Mondal and co-workers [60] prepared NiCo₂O₄ nanosheets by a facile microwave method with the specific capacitance of 560 F/g at 2 A/g and superior cycling stability over 5000 cycles (the capacitance loss was 4.8%). Cheng et al. [82] fabricated novel nanocyclobenzene NiCo₂O₄ nanosheets on nickel foam (as shown in Figure 7c) with a high specific capacitance of 1545 F/g at a current density of 5 A/g and long-term cyclic stability (93.7% capacitance retention after 5000 cycles) in 2 M KOH aqueous solution.

2.2.3. 3D NiCo₂O₄ Spheres

The vastly reported 3D NiCo₂O₄ further reflects its controllable morphologies. 3D NiCo₂O₄ nanostructures retained a large amount of space between neighboring structures, which greatly enlarge the specific surface area and provide a large volume of 3D continuous electron transport channels for electrolyte ion accumulation by acting as an ion reservoir. Moreover, 3D NiCo₂O₄ nanostructures tend to possess more stable structures. What is more, it is feasible to combine other low dimensional materials to synthesized 3D nanostructures, which exhibit intriguing synergistic

effects. Wang et al. [33] successfully fabricated urchin-like NiCo_2O_4 via a facile hydrothermal method without any template and catalyst, which was formed by numerous small nanorods with diameters of 100–200 nm and lengths of about 2 μm radially grown from the center, as shown in Figure 8a. Further studies revealed that the morphologies of the products could be adjusted by urea, and the morphologies transformed from rods via bundles to urchins with the values of pH from 5.5 to 6.8. These urchin-like NiCo_2O_4 structures possessed large surface areas ($99.3 \text{ m}^2/\text{g}$), and the specific capacitance reached 1650 F/g at 1 A/g with the capacitance loss of about 9.2% after 2000 cycles. Wu et al. [83] and Zou et al. [44] also reported the syntheses of urchin-like NiCo_2O_4 structures with superior electrochemical performances, as shown in Figure 8b,c, which were constructed by one-dimensional nanowires. In addition, by employing a rapid and template-free microwave-assisted heating (MAH) reflux approach followed by pyrolysis of the as-prepared precursors, Lei and co-workers [54] obtained 3D hierarchical flower-shaped spinel NiCo_2O_4 microspheres, as depicted in Figure 8d, which possess a large specific surface area ($148.5 \text{ m}^2/\text{g}$, pore size 5–10 nm), high specific capacitance (1006 F/g at 1 A/g and 726 F/g at 20 A/g) and superior electrochemical stability (93.2% after 1000 cycles). Similar 3D flower-like hierarchitectures were also reported by other groups (Figure 8e) [39,84,85]. Li et al. [38] assembled NiCo_2O_4 double-shell hollow spheres by engaging carbon spheres as the template, as shown in Figure 8f. Compared with single-shell NiCo_2O_4 hollow spheres, double-shell NiCo_2O_4 hollow spheres possessed enlarged surface areas of $115.2 \text{ m}^2/\text{g}$ from $76.6 \text{ m}^2/\text{g}$ and improved specific capacitance of 568 F/g from 445 F/g at 1 A/g. Furthermore, they improved the electrical conductivity of these NiCo_2O_4 hollow spheres by annealing the samples at 300 °C in hydrogen for 1.5 h, and the specific capacitance was simultaneously enhanced to be 718 F/g at a current density of 1 A/g. However, the template of carbon spheres used in this work would increase the costs, which would not be beneficial to large commercialization. Shen et al. [62] used a facile way to synthesize NiCo_2O_4 core-in-double shell hollow spheres with uniform NiCo-glycerate precursor and followed a simple non-equilibrium heat treatment process (Figure 8g). The specific capacitances were 1141, 1048, 965, 862 and 784 F/g at current densities of 1, 2, 5, 10 and 15 A/g, respectively, and there was only a 5.3% loss after 4000 cycles, indicating the favorable cycling stability.

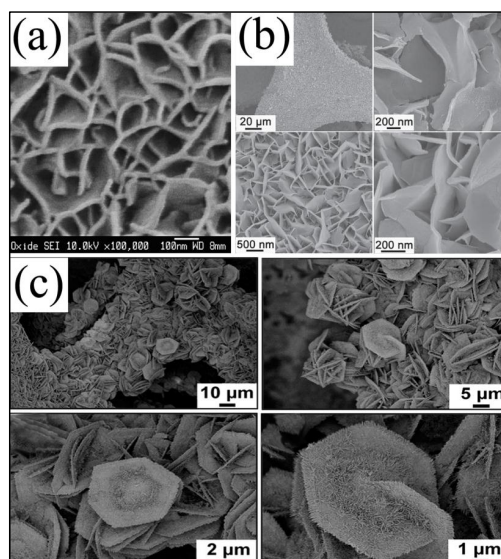


Figure 7. SEM images at different magnifications: (a) NiCo_2O_4 nanosheets on stainless-steel (Reproduced with permission from [45]. Copyright Elsevier, 2010); (b) NiCo_2O_4 nanosheets on Ni foam (Reproduced with permission from [49]. Copyright John Wiley and Sons, 2013); (c) NiCo_2O_4 nanocyclobenzene arrays on Ni foam (Reproduced with permission from [82]. Copyright the Royal Society of Chemistry, 2014).

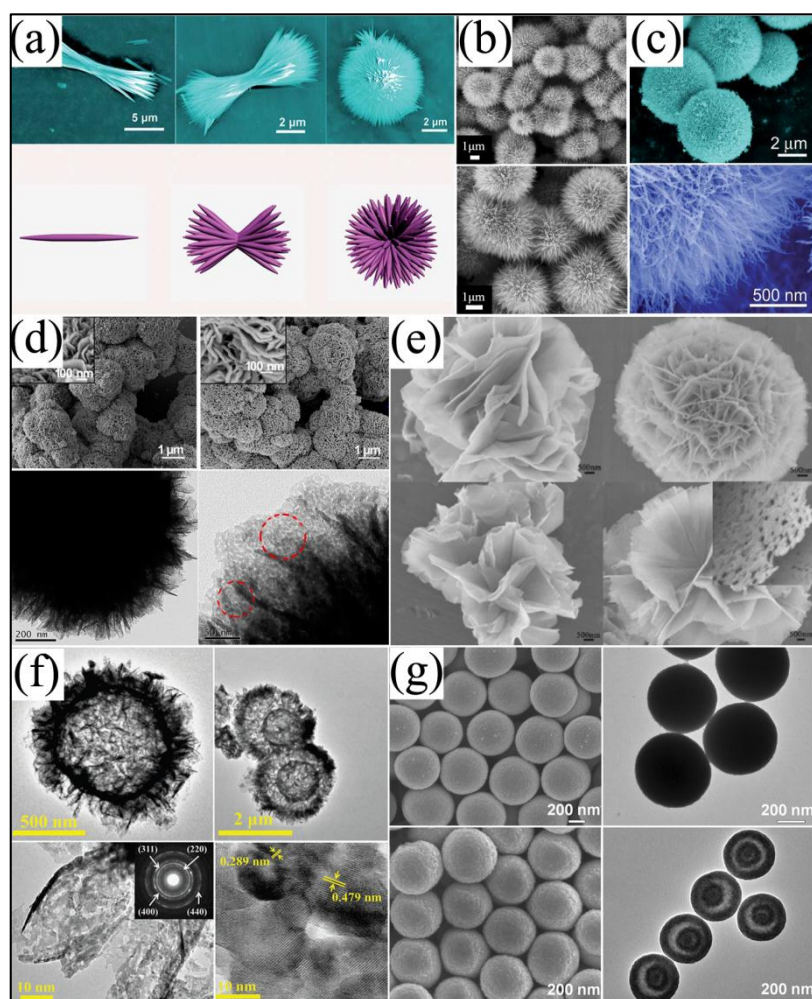


Figure 8. (a) SEM images of the NiCo_2O_4 products under different pH values and schematic illustrations of the growth mechanism of the urchin-like NiCo_2O_4 nanostructures (Reproduced with permission from [33]. Copyright the Royal Society of Chemistry, 2012); (b) urchin-like NiCo_2O_4 microspherical superstructures (Reproduced with permission from [83]. Copyright Elsevier, 2012); (c) SEM image of as-synthesized NiCo_2O_4 micro-spheres (Reproduced with permission from [44]. Copyright the Royal Society of Chemistry, 2013); (d) SEM and TEM images of as-fabricated NiCo_2O_4 (Reproduced with permission from [42]. Copyright American Chemical Society, 2014); (e) SEM images of as-prepared materials (Reproduced with permission from [39]. Copyright American Chemical Society, 2015); (f) TEM images of single-shelled and double-shelled NiCo_2O_4 spheres (Reproduced with permission from [38]. Copyright Nature Publishing Group, 2015); (g) typical FESEM and TEM images of NiCo_2O_4 (Reproduced with permission from [62]. Copyright John Wiley and Sons, 2015).

2.3. NiCo_2O_4 -Based Composites Nanostructures

Composite materials have received increasing concern, which was mainly due to the superior performance compared to solitary materials induced by the synergistic effect. In addition to pure NiCo_2O_4 nanostructures, NiCo_2O_4 -based composites have also been intensively investigated as electrode materials for supercapacitors. Therefore, in this section, we will review the NiCo_2O_4 -based composites containing carbonaceous materials and TMO/Hs, etc., as listed in Table 2.

2.3.1. The Combination of NiCo_2O_4 -Based Materials with Carbonaceous Materials

Due to the high specific-area, good electrical conductivity and high chemical stability, carbonaceous materials, including graphene, carbon nanotubes, etc., have been typically used to

assemble NiCo_2O_4 -based composite electrodes. Additionally, carbon materials can be obtained by carbonizing the organics, which can be used to recycle waste materials into profitable materials and a benefit to the environment. For instance, Xiong et al. [86] fabricated mollusk shell-based macroporous carbon material (MSBPC) by carbonizing the organic matrix of mollusk shell, as shown in Figure 9a, which was treated as the conductive scaffolds growing NiCo_2O_4 nanowires as supercapacitor electrodes. The electrodes of NiCo_2O_4 /MSBPC composites exhibited superior high specific capacitance (1696 F/g, at the current of 1 A/g), excellent rate performance (maintained 58.6% at 15 A/g) and outstanding cycling stability (still remained 88%, after 2000 cycles). The hexangular and tightly-arranged channels of the MSBPC promoted the efficient penetration of electrolyte and fast electron transfer, which could be responsible for the excellent performance. Significantly, carbon nanotubes (CNT) [35,63,87] and graphene/reduced graphene oxide (RGO) [68,88–91] have also been employed to assemble composite with NiCo_2O_4 nanomaterials. For example, Nguyen et al. [68] fabricated three-dimensional nickel foam/graphene/ NiCo_2O_4 , which displayed a higher specific capacitance of 1950 F/g at 7.5 A/g; Wang et al. [90] reported RGO/ NiCo_2O_4 nanoflakes with a high performance of 1693 F/g at 1 A/g; Wu et al. [35] synthesized 3D Ni foam/N-CNT/ NiCo_2O_4 nanosheets with superior supercapacitive performances of 1472 F/g at 1 A/g.

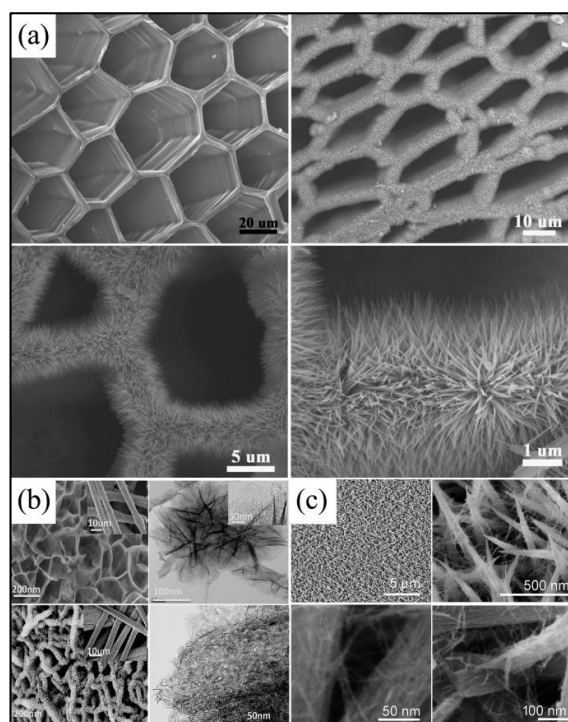


Figure 9. (a) SEM images of the NiCo_2O_4 /mollusk shell-based macroporous carbon (MSBPC) composites (Reproduced with permission from [69]. Copyright American Chemical Society, 2014); (b) SEM and TEM images of carbon fiber paper (CFP) after the growth of NiCo_2O_4 nanosheets and $\text{Ni}(\text{OH})_2/\text{NiCo}_2\text{O}_4$ nanosheets on CFP (Reproduced with permission from [86]. Copyright American Chemical Society, 2013); (c) As-synthesized networked $\text{NiCo}_2\text{O}_4/\text{MnO}_2$ branched nanowire heterostructure (BNH) arrays on Ni foam (Reproduced with permission from [92]. Copyright the Royal Society of Chemistry, 2015).

Table 2. NiCo₂O₄-based composites nanostructures.

| Materials | Preparation Methods //Annealing Condition | Specific Capacitance //Loading Mass | Rate Performance | Capacity Retention | GCD Potential Window//Electrolyte | Ref. |
|--|--|---|---|---|--------------------------------------|------|
| carbon nanotube/NiCo ₂ O ₄ | electrochemical deposition //300 °C/2 h | 694 F/g (at 1 A/g) | 82% (at 20 A/g) | 91% (1500 cycles) | 0–0.41 V vs. SCE// 6 M KOH | [63] |
| NiCo ₂ O ₄ @Co _x Ni _{1-x} (OH) ₂ | electrochemical deposition //300 °C/2 h | 5.71 F/cm (at 5.5 mA/cm ²) (x = 0.33) //5.5 mg/cm ² | 83.7% (at 273 mA/cm ²) (x = 0.33) | 80% (3000 cycles) (at x = 0.33) | –0.15–0.45 V vs. SCE// 1 M KOH | [67] |
| graphene/NiCo ₂ O ₄ | electrochemical deposition //300 °C/2 h | 15 mg/cm ² | 1950 F/g (at 7.5 A g ⁻¹) | 92.8% (10,000 cycles) | –0.1–0.3 V vs. SCE// 3 M KOH | [68] |
| Ni(OH) ₂ @NiCo ₂ O ₄ | electrochemical deposition// 300 °C/2 h | 5.2 F/cm 3200 F/g (at 2 mA/cm ²) //0.6 mg/cm ² | 79% (at 50 mA/cm ²) | 36% (1000 cycles) | 0–0.45 V vs. SCE// 1 M KOH | [69] |
| NiCo ₂ O ₄ @polypyrrole nanowires | hydrothermal 110 °C/12 h //300 °C/2 h in air | 2055 F/g (at 1 A/g) //1.67 mg | 742 F/g (at 50 A/g) | 90% (5000 cycles) | –0.2–0.45 V vs. SCE// 3 M NaOH | [93] |
| NiCo ₂ O ₄ nanowires/ mollusc shell based macroporous carbon | hydrothermal 110 °C/12 h //300 °C/2 h | 1696 F/g (at 1 A/g)// 1.5 mg/cm ² | 24.9% (at 50 A/g) | 88% (2000 cycles) | 0–0.4 V vs. SCE// 2 M KOH | [86] |
| NiCo ₂ O ₄ @graphene nanoarchitectures | hydrothermal 90 °C/12 h //350 °C/2 h | 778 F/g (at 1 A/g) | 48% (at 80 A/g) | 90% (10,000 cycles) | 0–0.5 V vs. SCE// 2 M KOH | [88] |
| NiCo ₂ O ₄ -RGO composite | self-assembly //800 °C/8 h in air | 835 F/g (at 1 A/g)//2 mg/cm ² | 615 F/g (at 20 A/g) | higher than the initial value (4000 cycles) | 0.1–0.5 V vs. Hg/HgO// 6 M KOH | [89] |
| CNT@NiCo ₂ O ₄ | precipitate //300 °C/3 h | 1038 F/g (at 0.5 A/g) | 64% (at 10 A/g) | 100% (1000 cycles) | –0.1–0.36 V vs. SCE// 6 M KOH | [87] |
| NiCo ₂ O ₄ @CoMoO ₄ | hydrothermal 120 °C/6 h //400 °C/3 h in air | 14.67 F/cm (at 10 mA/cm ²) //2.3 mg/cm ² | 65.8% (at 60 mA/cm ²) | 89.3% (1000 cycles) | –0.1–0.5 V vs. SCE// 2 M KOH | [94] |

Table 2. Cont.

| Materials | Preparation Methods //Annealing Condition | Specific Capacitance //Loading Mass | Rate Performance | Capacity Retention | GCD Potential Window//Electrolyte | Ref. |
|--|---|--|---|---|--------------------------------------|-------|
| Co ₃ O ₄ /NiCo ₂ O ₄ double-shelled nanocages | template 70 °C/10 h //350 °C/2 h | 972 F/g (at 5 A/g) //1 mg/cm ² | 63.2% (at 50 A/g) | 92.5% (12,000 cycles) | 0–0.42 V vs. SCE// 1 M KOH | [95] |
| NiCo ₂ O ₄ @MnO ₂ nanowire arrays | hydrothermal 120 °C/6 h //300 °C/2 h | 2.224 F/cm ² (at 2 mA/cm ²) //1.2 mg/cm ² | 55.3% (at 50 mA/cm ²) | 113.6% (8000 cycles) | 0–0.45 V vs. SCE// 1 M NaOH | [96] |
| NiCo ₂ O ₄ @MnO ₂ core-shell nanowire arrays | hydrothermal 90 °C/8 h //350 °C/2 h | 3.31 F/cm ² (at 2 mA/cm ²) //1.4 mg/cm ² | 1.66 F/cm ² (at 20 mA/cm ²) | 88% (2000 cycles) | 0–0.6 V vs. SCE// 1 M LiOH | [97] |
| NiCo ₂ O ₄ @NiCo ₂ O ₄ nanoflake arrays | hydrothermal 120 °C/3 h //350 °C/2 h in argon | 1.55 F/cm ² (at 2 mA/cm ²) //1.97 mg/cm ² | 1.16 F/cm ² (at 40 mA/cm ²) | 98.6% (4000 cycles) | 0–0.55 V vs. Hg/HgO// 2 M KOH | [98] |
| NiCo ₂ O ₄ @Ni ₃ S ₂ nanothorn arrays | hydrothermal 85 °C/9 h //350 °C/3 h in air | 1716 F/g (at 1 A/g) //2.1 mg/cm ² | 1104 F/g (at 20 A/g) | 83.7% (2000 cycles) | 0–0.5 V vs. Hg/HgO/ 2 M KOH | [99] |
| nickel-cobalt double hydroxide nanosheets on NiCo ₂ O ₄ nanowires (x = 0.67) | hydrothermal 120 °C/16 h (x = 0.67) //300 °C/2 h in air | 1.64 F/cm ² (at 2 mA/cm ²) (x = 0.67) //1 mg/cm ² | 67.55% (at 90 mA/cm ²) (x = 0.67) | 81.3% (2000 cycles) (x = 0.67) | –0.1–0.45 V vs. SCE// 1 M KOH | [100] |
| carbon–CoO–NiO–NiCo ₂ O ₄ nanosheet hybrid hetero-structured arrays | hydrothermal 120 °C/6 h //350 °C/3 h | 5.23 F/cm ² 2602.0 F/g (at 2 mA/cm ²) //2 mg/cm ² | 76.1% (at 50 mA/cm ²) | higher than the initial value (7000 cycles) | 0–0.48 V vs. SCE// 6 M KOH | [101] |
| sponge-like NiCo ₂ O ₄ /MnO ₂ ultrathin nanoflakes | electrochemical deposition //250 °C/2 h | 935 F/g (at 1 A/g) //0.55 mg/0.4 cm ² | 74.9% (at 50 A/g) | 103.1% (25,000 cycles) | –0.1–0.5 V vs. Ag/AgCl// 1 M KOH | [102] |
| NiCo ₂ O ₄ /MnO ₂ branched nanowire heterostructure arrays | hydrothermal 180 °C/8 h //300 °C/2 h in air | 2827 F/g (at 2 mA/cm ²) //0.92 mg/0.4 cm ² | 66.8% (at 100 mA/cm ²) | 98.4% (3000 cycles) | 0–0.5 V vs. SCE// 1 M KOH | [92] |

2.3.2. The Combination of NiCo₂O₄-Based Materials with TMO/Hs

Since spinel NiCo₂O₄ possesses high electronic conductivity and controllable morphologies, it is of great significance to use the spinel NiCo₂O₄ structures as the conductive scaffold to synthesize other TMO/Hs materials or deposit NiCo₂O₄ structures to other materials in the expectation of synthesizing smart architectures to realize a strong synergistic effect for high performance supercapacitors. For example, Huang et al. [69] successfully fabricated NiCo₂O₄ nanosheets loading Ni(OH)₂ nanosheets as supercapacitor electrodes, as depicted in Figure 9b, which were grown on carbon fiber paper (CFP) by a facile two-step electrodeposition. By comparing Ni(OH)₂/NiCo₂O₄/CFP with Ni(OH)₂/Co₃O₄/CFP, they discovered that 3D hybrid composite Ni(OH)₂/NiCo₂O₄/CFP electrodes demonstrated higher performance with 5.2 F/cm² (3200 F/g) at 2 mA/cm², which were most likely due to the higher conductivity of NiCo₂O₄ than Co₃O₄. However, the specific surface area of the Ni(OH)₂/NiCo₂O₄/CFP decreased more than 80% after 1000 cycles; meanwhile, the areal capacitance dropped over 64% after 1000 cycles. Zou and co-workers [92] prepared networked NiCo₂O₄/MnO₂ branched nanowire heterostructure (BNH) arrays on Ni foam substrates, as shown in Figure 9c. The specific capacitances of the NiCo₂O₄/MnO₂ BNH were as high as 2827 F/g at 2 mA/cm² and 1891 F/g at 100 mA/cm², and the overall capacitance loss of the initial product is only 1.6% after 3000 cycles, indicating the excellent cycling stability.

In addition to the carbonaceous materials and TMO/Hs, the spinel NiCo₂O₄ has been widely employed as a conductive scaffold and been used to assemble composites with other materials, such as conductive polymers [86,103], transition metal sulfide [99,104], TiN [105] and halloysite nanotubes [51].

It is of great significance to combine the NiCo₂O₄ with other materials, which induced synergistic performance to further improve the supercapacitive performance. However, many composites suffer from a complicated fabrication process. Therefore, it is feasible to simplify the synthesis process to optimize the performance and cost.

3. Conclusions

Supercapacitors cover the power gap between batteries and conventional dielectric capacitors with higher energy density than conventional dielectric capacitors and larger power density than batteries, which carry much expectation for next-generation energy storage devices due to their high power densities, long cycling lifespans and fast charge/discharge processes. Since the performance was greatly influenced by the electrode materials, it is significant to endeavor to enhance the electrode performance. In this review, we summarized the syntheses and the performance of supercapacitor electrodes of spinel NiCo₂O₄ and its composites with various morphologies. Owing to the easy controllability on the morphologies of NiCo₂O₄, many architectures, from 1D nanorods/nanowires, 2D nanosheets/nanoplates and to 3D structures, have been fabricated. The displayed excellent supercapacitive performance can be ascribed to the higher electronic conductivity, electrochemical activity and the richer faradic redox reactions in alkaline electrolytes. Additionally, the robust spinel NiCo₂O₄ structures have been widely employed as scaffolds to grow other composite materials.

Although the spinel NiCo₂O₄ demonstrates remarkable properties, there still are many challenges to overcome before commercialization. Firstly, the supercapacitive mechanisms of the NiCo₂O₄ still lack agreement about whether NiCo₂O₄ can be classified as pseudocapacitor materials. Though almost all of the literature for supercapacitors of the spinel NiCo₂O₄ declared that this material was a pseudocapacitor material, NiCo₂O₄, as a well-known battery-type electrode material, has not been designated as a pseudocapacitive material. It is better for there to be agreement about the spinel NiCo₂O₄ material as a hybrid supercapacitor or battery-type supercapacitor. Secondly, the theoretical capacitance of spinel NiCo₂O₄ materials would be clearly given, and the causes for the differences of the same material being so great should be further expatiated, instead of explaining them merely from morphologies and structures. Thirdly, the narrow potential window of the spinel NiCo₂O₄ in alkali electrolyte (only approximately 0.45 V–0.5 V, as shown in Tables 1 and 2) means lower energy and power density. Then, it is dramatically significant to assemble an asymmetric device

by combining NiCo₂O₄-ased materials with the carbonaceous materials possessing a wide potential window. Fourthly, it is better to have a uniform standard about the electrodes' preparation, especially on the mass loading of active material, which should be combined with the commercial application. Fifthly, it is unwise to sacrifice the power density to improve the energy density, which requires the balance between them. Sixthly, although the performances of NiCo₂O₄ are greatly dominated by the morphology, it is feasible to develop other similar nanomaterials, such as NiCo₂S₄, to further improve the performance because of its even higher conductivity [106–108]. Finally, the self-discharge of the supercapacitors should have enough attention paid to it and be included in the evaluation of supercapacitors.

All in all, we firmly believe that the supercapacitors will have tremendous developments, and the spinel NiCo₂O₄ as a supercapacitor material will be commercialized in the near future, which possesses supercapacitors' high power density and batteries' high energy density.

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Abbreviations

| | |
|----------|------------------------------------|
| EDLCs | Electrical double-layer capacitors |
| PCs | Pseudocapacitors |
| TMO/Hs | Transition metal oxides/hydroxides |
| ESR | Equivalent series resistance |
| K_{sp} | Solubility constant |
| SCE | Saturated calomel electrode |
| SEM | Scanning electron microscope |
| TEM | Transmission electron microscope |
| SAED | Selected area electron diffraction |

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