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Review article

A review of synthesis strategies for nickel cobaltite-based composites in supercapacitor applications

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ABSTRACT

Supercapacitors (SCs), known for their exceptional power and reasonably high energy densities, long lifespan, and lower production costs, have emerged as an ideal solution to meet the growing demand for various energy storage applications. The characteristics of supercapacitors are greatly influenced utilizing the choice of electrode materials, developing novel electrode materials a focal point for extensive research in the field of high-performance supercapacitors. In recent years, $NiCo_2O_4$ has garnered increasing attention as a supercapacitor electrode material owing to its notable edges, including high theoretical capacity, low cost, abundant availability, and ease of synthesizing. However, the performance of $NiCo_2O_4$ is hindered by its low electrical conductivity and limited surface area, leading to significant capacity deterioration. Therefore, it is imperative to systematically and comprehensively summarize the advancements in comprehending and adjusting $NiCo_2O_4$-based electrodes from multiple perspectives. The present review primarily focuses on the synthetic approaches employed to produce $NiCo_2O_4$ nanomaterials with diverse morphologies for their application in supercapacitors. This review article provides a comprehensive overview of the synthesis approaches utilized for developing nickel cobaltite-based composites tailored for supercapacitor applications. Various synthesis methods, including sol-gel, hydrothermal, and co-precipitation techniques, are discussed in detail, emphasizing the importance of optimizing synthesis parameters to enhance the electrochemical performance of the composites. The potential applications of nickel cobaltite-based composites in supercapacitors are explored, highlighting their promising prospects in energy storage technologies. Future research directions in this field are also discussed.

KEYWORDS

Supercapacitor
$NiCo_2O_4$
Energy storage
Synthesis
Electrode

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1. Introduction

The utilization of electronic gadgets and the associated demands for electronic devices have escalated in contemporary society, leading to a plethora of energy and environmental predicaments. These predicaments encompass pollution, the dearth of fossil fuels, and the escalating issue of global warming. To surmount these multifarious issues, there is an absolute necessity for eco-friendly and durable energy materials, along with the accompanying devices [1, 2].

Fortunately, the utilization of sustainable energy sources such as solar and wind energy has been significantly enhanced in our daily lives. However, the intermittent character of these renewable energy sources necessitates developing energy storage devices that possess exceptional performance [3]. Electrochemical energy storage (EES) devices, including batteries, fuel cells, and supercapacitors (SCs), emerge as the most encouraging systems with the capacity to fulfill both present and future energy requirements [4, 5]. Most notably, these devices have the capacity to effectively retain electrical potential in the shape of

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chemical potential and convert the retained potential into electrical potential in a reversible manner, thereby avoiding any concerns related to environmental contamination [6]. Most batteries experience a deficiency in power delivery and are incapable of meeting the increased demands for faster and higher-power energy. On the other hand, supercapacitors have the ability to effectively bridge the power-energy disparity that exists among traditional dielectric capacitors, which offer substantial batteries, and power output, and possess a great energy density [7].

Over the past four decades, there has been a significant amount of attention directed towards Supercapacitors. This can be attributed primarily to their long lifecycles, impressive power density, and their capability to address the power/energy disparity found in dielectric capacitors. The latter is due to their ability to store substantial amounts of energy and produce considerable power output [8]. The performance of supercapacitors encompasses various dimensions, namely operational voltage, specific capacity, specific energy and power density, and cyclic life [9]. It has been widely documented that the capability of supercapacitors to store energy, is linked directly to the electrode materials. Concerning a fascinating supercapacitor, the paramount importance of electrode materials is essential for the environmentally friendly, highly effective, and adaptable utilization of energy. Several research endeavors have been undertaken to fabricate proficient electrode materials for supercapacitors (SCs) to attain elevated specific capacitance coupled with praiseworthy energy densities [10].

Different types of materials, including metal oxides [11], conducting polymers [12], and carbon-based materials [13], have been extensively studied as potential materials for supercapacitor electrodes [14]. The utilization of carbonic materials offers advantages such as high specific surface area and conductivity, contributing to achieving high power density. Still, their drawback lies in their limited energy density and practical applications [15]. Similarly, conducting polymers like polypyrrole and polyaniline, as well as transition metal oxides such as NiO, CO_3O_4, and MnO_2, have exhibited enhanced energy density. Yet, their long-standing cycling life remains a challenge [16].

Recently, a noteworthy number of researches have been focused on ternary metal oxides. These oxides exhibit exceptional specific capacity and excellent electrical conductivity, surpassing that of single-component oxides. This superiority can be attributed to their ability to achieve multiple oxidation states for various redox reactions [17]. The distinctive cobaltite, for instance, follows $Co^{2+}_{1-x}Co^{3+}_x[Co^{3+}Ni^{2+}_xNi^{3+}_{1-x}]O_4$ ($0 < x < 1$) as a widespread formula [18]. In this compound, the Ni sites are at the octahedral positions, while the Co species are speared across both octahedral and tetrahedral locations. By combining two different metal cations in the $A_xB_{3-x}O_4$ formula, the redox reactions are improved, leading to enhanced electrical conductivity (more than twice that of Co or Ni oxide alone) [19]. This improvement is due to the introduction of additional electrons into the 3d orbital through the replacement of Co with Ni. Consequently, this substitution subtly alters the electron density in the crystal structure, thereby proving advantageous for the application of SCs [20]. It is additionally, it has been confirmed that $NiCo_2O_4$ owned a considerably lower resistance than cobalt monoxides as well as nickel oxides. Throughout the charge storage procedure, M_3O_4 (M=Co or Ni) follows the subsequent equation [21].

$$M_3O_4 + OH^- + H_2O \leftrightarrow 3MOOH + e^- \quad (1)$$

Therefore, $NiCo_2O_4$ has emerged as a highly auspicious and flexible substitute for electrode material implementation in supercapacitors with high-performance capabilities, consequently garnering escalating interest in recent years. The poor rate capability and electrochemical reversibility of $NiCo_2O_4$ electrodes stem from the inherent characteristics of the redox reaction. Numerous effective approaches have been documented to address this issue. Various factors such as electrolyte composition, pH levels, temperature, surfactant presence, aging duration, synthesis techniques, etc., are crucial in controlling the morphology and electrochemical properties of electrode materials [22]. Here, delve into the structure and synthesis technique of $NiCo_2O_4$-based materials, providing an extensive examination. Subsequently, the primary goal of this review is to accentuate the novel advancements in utilizing the anticipated approaches to enhance the rate capacity and the cycling life of materials based on $NiCo_2O_4$. This includes the synthesis process, and manipulation of distinctive morphologies.

2. Crystal structure of $NiCO_2O_4$

$NiCo_2O_4$ is known as a cost-efficient ternary metal oxide, contributed from both nickel and cobalt ions, which causes better electrical conductivity (2×10 S.cm^{-1}) than the cobalt oxides (333 S.cm^{-1}) or single nickel (2×10^{-2} S.cm^{-1}) component. As Fig. 1 depicts, $NiCo_2O_4$ as a material with a spinel structure has a face-centered cubic conformation. In this structure, Ni and Co cations are located at one-eighth of the tetrahedral and one-half of the octahedral positions while residual tetrahedral and octahedral sites are occupied by O anion [23]. Two-third of the cations have 3+ oxidation and the remaining have 2+ oxidation states. Notably in $NiCo_2O_4$ structure, octahedral locations can be occupied by both Ni and CO but the tetrahedral positions cannot be occupied by Ni. The resulting varied valence states of cations promise better redox chemistry and also afford twice the electrical conductivity of a single oxide, which causes enhanced capacity of charge storage. Ternary metal oxides possess higher electrical conductivity than binary compounds. Ternary metal oxides benefit from better electrical conductivity than binary compounds. During the redox procedure, the process of charge storing of $NiCo_2O_4$ in an alkaline medium refers to the reversible reactions of Co^{2+}/Co^{3+} and Ni^{2+}/Ni^{3+} conversions which are given below [19]:

$$NiCo_2O_4 + OH^- + H_2O \leftrightarrow 3NiOOH + 2CoOOH + 2e^- \quad (2)$$

The rapid reactions involving the transformation of Co^{3+} to Co^{4+} and Ni^{2+} to Ni^{3+} occur during the process of charge-discharge on the electrode surface. The redox potentials for the conversion of Co^{3+} to Co^{4+} and Ni^{2+} to Ni^{3+} are near one another, resulting in their redox peaks overlapping. The general electrochemical performance of $NiCo_2O_4$ as a supercapacitor electrode is affected pivotally by the crystal structure which is in conjunction with the material morphology [24].

3. $NiCo_2O_4$ synthesis methods

Accompanied by a diverse range of physical characteristics, such as morphology, porosity, and textures, $NiCo_2O_4$ exhibits a multitude of diverse electrochemical characteristics. The surface morphology and crystal structure of this compound are closely connected to its electrochemical behavior. Researchers and industry professionals are hopeful for developing advanced $NiCo_2O_4$-based electrode materials with distinctive nanostructures and efficient performance. However,

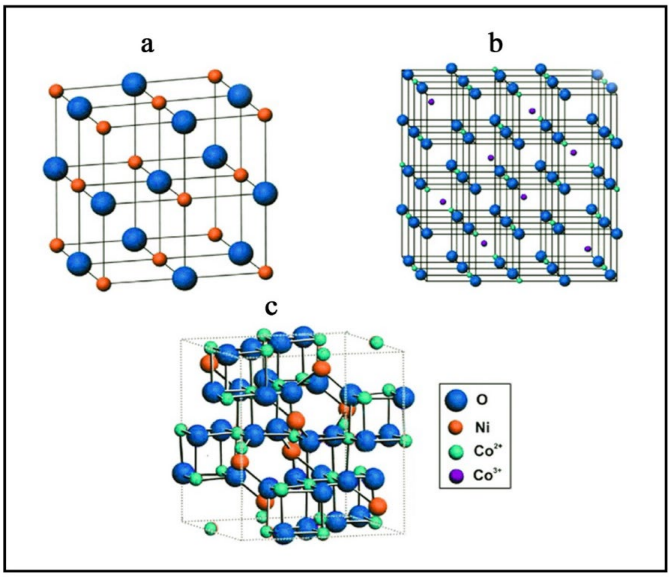

Fig. 1. Crystal structures of a) NiO, b) Co_3O_4, and c) $NiCo_2O_4$ unit cells.

synthesizing all types of $NiCo_2O_4$ nanomaterials universally and cost-effective manner poses significant challenges. In general, extensive efforts have been made to adjust the synthesis conditions to obtain desired morphologies and enhance the electrochemical characteristics of $NiCo_2O_4$. These methods are thoroughly summarized and discussed in the present review.

3.1. Sol-gel method

The nomenclature sol-gel is derived from the observation that molecules or micro-particles within a solution (sol) aggregate and eventually coalesce under controlled circumstances to yield a cohesive network (gel). This methodology represents a facile synthesis technique for generating nanostructures possessing the desired characteristics of uniformity, porosity, and high degree of purity. The sol-gel procedure typically encompasses four sequential stages: 1) precursor solution fabrication, 2) sol formation resulting in intermediate products, 3) conversion from sol to gel, and subsequently 4) calcination. Throughout this process, the choice of solvents, reaction temperature, reaction duration, and surfactants play pivotal roles in achieving the intended structures, characterized by exceptional electrochemical properties [25]. The sol-gel technique manifests two primary variations: colloidal and polymeric (or alkoxide) routes [26]. Sol-gel methods are widely recognized as one of the preferred techniques for synthesizing high-performance electrode materials due to their numerous benefits such as homogeneity and purity in products, low-temperature synthesis, facile generation of diverse morphologies, cost-effectiveness, ease of implementation, and creation of very fine powders with high specific surface [27, 28]. The sol-gel method has a higher popularity and industrial application than other existing methods. Several critical factors, including the initial concentration of reactants, reaction time, and solvent species, are crucial in influencing the final morphology of the prepared $NiCo_2O_4$ with a facile sol-gel approach [29]. Chelating agents play a very important role in the sol-gel process, agents like citric acid (CA), oxalic acid (OA), and ethylenediamine tetraacetic acid (EDTA) effect on particle size, pore structure, and specific surface area of the $NiCo_2O_4$ which can exert a great influence on the electrochemical properties [30, 31].

For instance, the sol-gel method has been utilized by Liu and co-workers [32] to fabricate $NiCo_2O_4$ aerogels. As shown in Fig. 2 the proposed procedure began with the dissolution of $Ni(NO_3)_2.6H_2O$ and $CoCl_2.6H_2O$ in ethanol and mixing and then addition of propylene oxide followed by stirring the mixture at room temperature. The resulting solution was then stirred to promote gelation. The product was dried and then heated in an air atmosphere. In the last step, ethanol and distilled water were used several times to wash the samples and then they dried. The gelation mechanism can be defined via the reaction provided in Fig. 2, where M refers to nickel or cobalt ions, and A^- corresponds to Cl^- or NO_3^- ions [32].

3.2. Hydrothermal and solvothermal method

Recently, the hydrothermal route has been regarded as a reassuring methodology for synthesizing nanostructures due to its environmentally friendly nature, as well as its ability to precisely control reaction conditions and produce a variety of nanostructures such as nanowires, nanosheets, and nanoflowers. The hydrothermal method entails heterogeneous reactions occurring in an aqueous context, under high-pressure conditions and typically at temperatures variety of 100 to 200 °C. Attain to these specific circumstances, typically, the reaction is conducted within Teflon-lined sealed steel autoclaves. With the aim of conversion of the metal salts precursor into their corresponding hydroxides, NH_3 or alkali metal hydroxide is utilized to introduce basic pH conditions. This process commences initially with the nucleation step which is followed by the deliberate growth of crystals across proper crystal planes. Surface characteristics and morphology as well as structural attributes of the hydrothermally synthesized materials are contingent upon various factors, including pH solution, temperature, concentration of precursors, solvent nature, and presence of templates. Furthermore, temperature plays a pivotal role in controlling the

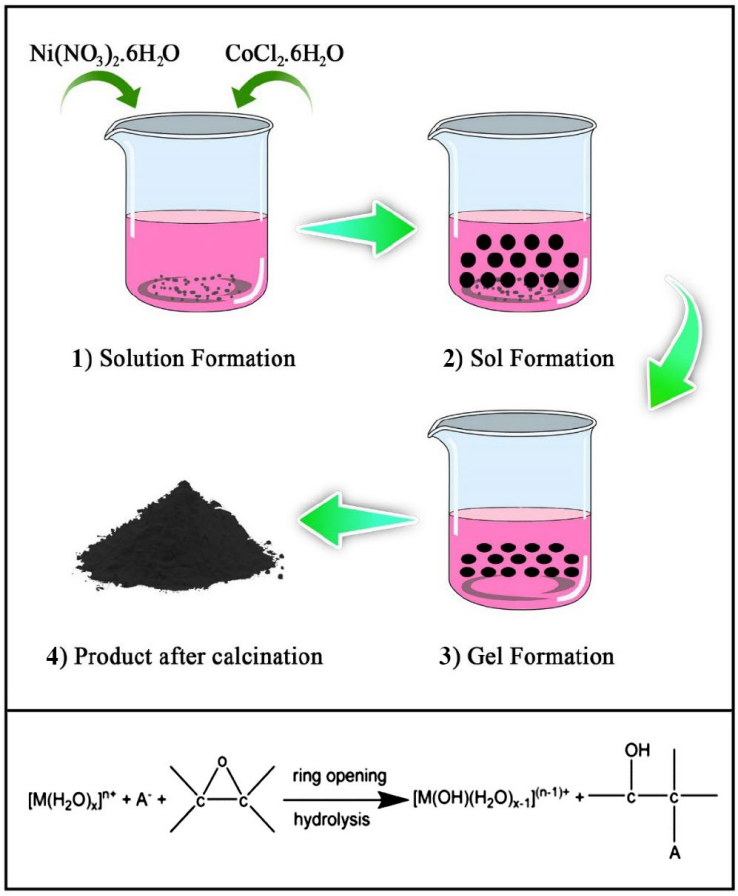

Fig. 2. Schematic diagram illustrating fabricating $NiCo_2O_4$ via the sol-gel process.

morphology of nanostructures during hydrothermal growth [33–35]. The hydrothermal method has been suggested as a viable technique for independently regulating the size of crystals [36].

The $NiCo_2O_4$ precursors were prepared through the employment of a hydrothermal reaction, wherein a relevant metal salts reagent mixture was subjected to heating in a sealed Teflon-lined stainless-steel autoclave. Given that the preparation of $NiCo_2O_4$ is a widely used technique, it is imperative to synthesize highly uniform nanoparticles with adjustable size and distinct morphology [37]. Zou et al. [38] conducted synthesizing $NiCo_2O_4$ using a typical hydrothermal method, as shown in Fig. 3. $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, and urea were dissolved in a solution consisting of ethanol and distilled water at room temperature. This resulted in the formation of a vivid pink solution under vigorous magnetic stirring. Subsequently, the obtained solution was transferred into a polytetrafluoroethylene (PTFE) (Teflon)-lined autoclave and placed in an electric oven. After undergoing cooling naturally to room temperature, the resulting sediment was collected and subjected to several rounds of washing using ethanol and deionized water through centrifugation. The precipitate was then dried overnight, to achieve a crystalline structure of nanoparticles, the initially synthesized $NiCo_2O_4$ precursor was thermally treated in an air atmosphere [38].

The synthesis of nanostructured materials using the hydrothermal method results in a highly porous structure, which is advantageous for facilitating large electrolyte-ion exchange in supercapacitors. Furthermore, this synthesis technique offers numerous benefits, including cost-effectiveness, uniform nucleation, and controlled grain growth [39].

Alternatively, the use of non-aqueous solvents provides an additional means of morphology engineering as well as optimizing porosity, and crystal growth across specific aligned nanomaterials crystal planes. This modified approach is referred to as solvothermal rather than hydrothermal. Notably, solvents with distinct polarities and solubilities can affect the degree of supersaturation degree, chemical species towards the crystal surface diffusion rates, and the interfacial surface energy, more than other factors [40]. For synthesizing $NiCo_2O_4$, a mixture of $NiSO_4.6H_2O$, $CoSO_4.7H_2O$, and CH_3CH_2OH was combined in distilled water and ethylene glycol (in a ratio of 1:1) with the assistance of ultrasonication. Subsequently, guanidine or urea was incrementally introduced into the aforementioned mixed solution, followed by stirring. The resulting mixture was then transferred into a Teflon-lined stainless-steel autoclave and maintained. Once the reactor had cooled to room temperature, the resulting precipitate was collected and subjected to multiple washes with deionized water and ethanol, followed by vacuum-drying. The material was then calcinated in an air atmosphere and subsequently placed in an oven. Additionally, an investigation was conducted to determine the influence of different solvents on the $NiCo_2O_4$ materials [41].

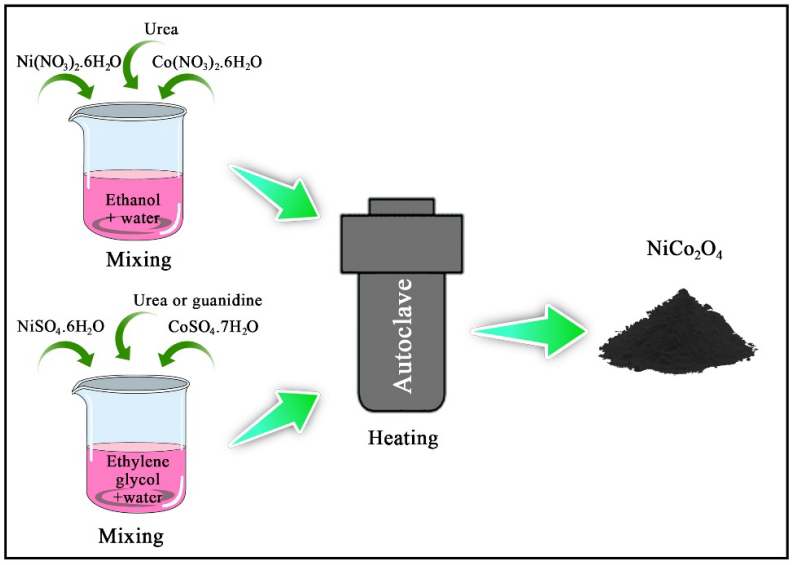

Fig. 3. Schematic illustration of the hydrothermal method for synthesis of $NiCo_2O_4$.

3.3. Template method

Mesoporous binary metal oxide synthesizing is a complex process owing to their thermal instability. Nevertheless, the advent of innovative synthesis approaches has led to the extensive adoption of the template method for creating mesostructured binary metal oxides. By utilizing template-based synthesis, the properties of nanostructures, such as their shape, size, morphology, and surface area, can be intentionally engineered to achieve controlled electrical, electronic physical, and chemical attributes. The overall growth process of nanostructures typically involves three steps: preparation of template, synthesizing of the favorable material via the template directly, and omission of the template. Several environmental factors, such as temperature growth, chemical nature, concentration, and structure, play crucial roles in influencing the growth of nanomaterials. The implementation of the template method can improve the stability of dispersion in reaction solutions. Furthermore, this method exhibits a significant increase in the reaction yield. The template synthesis method offers numerous advantages, including cost-effectiveness, ease of synthesis, and eco-friendliness. Various template-based methodologies have been reported for the $NiCo_2O_4$ nanomaterials synthesizing, resulting in adjustable morphologies such as nanocages [42], hollow spheres [43], nanospheres [44], hollow submicron spheres [45], hollow irregular octahedra-like cages, flower-like nanostructures [46], highly ordered mesoporous microspheres, nanowires, and others [47, 48].

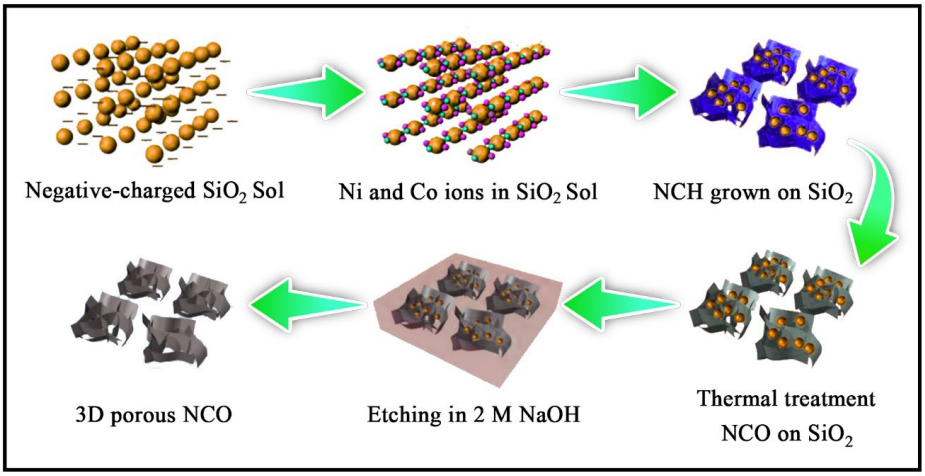

Fig. 4. The schematic illustration for the synthesis of silica particles via stöber method and formation of 3D porous $NiCo_2O_4$ nanoparticles.

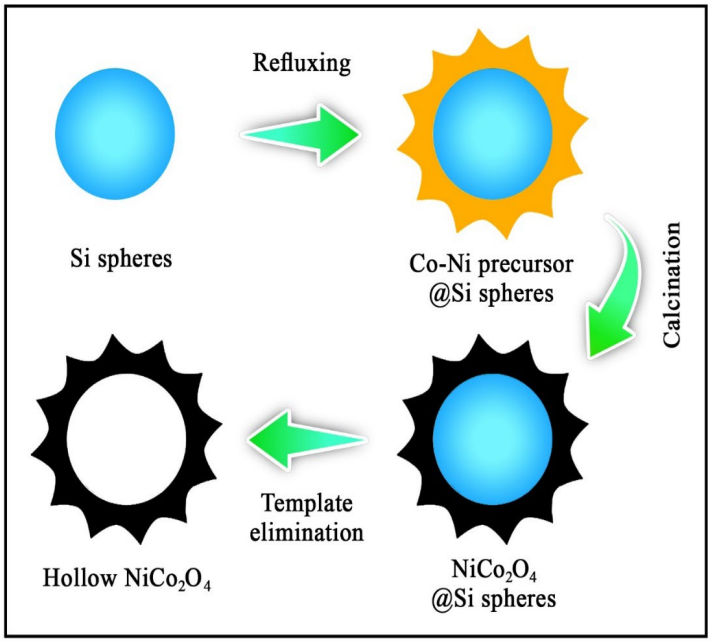

Fig. 5. Steps of formation of hollow $NiCo_2O_4$ nanoparticles through template method.

To begin the synthesis of $NiCo_2O_4$ via the template method, silica particles were synthesized using a modified stöber method. In the standard experimental procedure, the addition of SiO_2 sol into distilled water was carried out gradually, while the mixture was gently stirred. Throughout the process shown in Fig. 5, the SiO_2 sol remained stable, and the observation of the Tyndall effect was made possible. Subsequently, a solution containing $Ni(NO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ in water was added drop by drop to the aforementioned SiO_2 sol. Following this, urea was carefully introduced. After thorough stirring, the resulting mixture underwent refluxing in an oil bath. The resultant product of the reaction was then subjected to filtration and successive washing with distilled water and ethanol before finally being dried and heated in an ambient air environment. The resulting products, possessing an earthy yellow coloration, were subjected to etching in an aqueous solution of NaOH, with the etch solution being refreshed at 30-minute intervals. After multiple iterations of this process, the desired 3D porous structure of $NiCo_2O_4$ was successfully obtained [49].

3.4. Electro-deposition

Electro-deposition is widely regarded as an exceedingly valuable, versatile, and adaptable instrument for the deposition of nanotubes, nanowires, nanosheets, nanofoils, and numerous well-organized transition metal oxides on conducting surfaces. Pulse plating, potentiostatic, and galvanostatic are the three primary methodologies engaged for electro-deposition. The fundamental rule of electro-deposition encompasses three stages, namely, the metal ions precursor solution preparation, co-electro-deposition, and final thermal decomposition. Lately, this method has been harnessed for the fabrication of spinel structures $NiCo_2O_4$ [50].

Yan et al. [51] prepared $NiCo_2O_4$ nanosheets through a combined technique of electro-deposition and thermal treatment (Fig. 6). At the beginning, vigorous magnetic stirring was utilized to produce a homogenous solution of $Ni(NO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ in water. At the next step, using a three-electrode system, the Ni–Co hydroxide precursors were electro-deposited through Ni foam at a steady potential

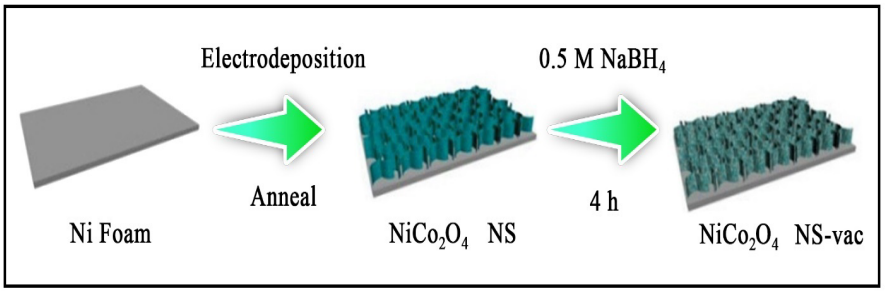

Fig. 6. Schematic illustration of the electrodeposition process for forming the $NiCo_2O_4$.

of -1.0 V (vs. SCE). After the process, this Ni-Co precursor was rinsed several times with DI water and dried. At last, the fabricated electrode was moved into annealing in an air atmosphere [51].

3.5. Electrospinning

Electrospinning is a comparably intricate but versatile and cost-effective method used for producing well-established nanofibers and nanotubes with dimensions ranging from several micrometers to tens of nanometers. Throughout the process of preparation, numerous significant factors have the potential to impact the shapes, diameters, and size distributions, of the nanofibers and nanotubes and, for instance, the metal precursor concentrations, the precursor solution viscosity, the polymer type, and different parameters the electrospinning (which include the solution feed rate, working distance, and the applied potential) [52]. Li et al. [53] assisted the electrospinning method for the synthesis of $NiCo_2O_4$, the precursor solution utilized for electrospinning was prepared through the dissolution of PVP in ethanol with vigorous stirring, resulting in the formation of a solution with a weight percentage of 10. Subsequently, equimolar amounts of $Co(Ac)_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$ were introduced into the solution, with a Co/Ni molar ratio of 2:1, to achieve a homogeneous and viscous solution. The precursor nanofibers were then subjected to electrospinning onto aluminum foil, which was obtained from the solution that was prepared earlier. A high voltage of 12 kV was applied between the aluminum collector and the needle tip, ensuring a distance of approximately 12 cm. The flow rate was maintained at a fixed value of 1 $ml.h^{-1}$. Finally, the compound $NiCo_2O_4$ was derived by subjecting the precursor nanofibers to calcination under an air atmosphere [53].

3.6. Co-precipitation method

The co-precipitation method offers a convenient means of attaining superior stoichiometric administration along with enhanced purity of metal oxide nanomaterials. This method involves the simultaneous precipitation of two or more cations from a homogeneous solution. The concomitant incidence of nucleation, growth, coarsening, Ostwald ripening, and aggregation significantly impacts different characteristics of the metal oxide nanoparticles, including morphology and size. It is worth noting that this technique has proven to be effective in synthesizing $NiCo_2O_4$ nanomaterials [54].

Zhang et al. [55] produced porous $NiCo_2O_4$ nanobelt through the utilization of a chemical co-precipitation technique in a water bath (Fig. 8). The water was mixed with $H_2C_2O_4.2H_2O$, which was subsequently dissolved. Additionally, $NiCl_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ were dissolved in de-ionized water. The washed Ni foam, by de-ionized water and HCl acid, was then submerged in a previously prepared solution of $H_2C_2O_4.2H_2O$ under the influence of electromagnetic stirring. The combined aqueous solution of $NiCl_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ was gradually introduced to the $H_2C_2O_4$ aqueous solution. Following this, the stirring procedure was carried out. The sample was thoroughly cleansed on multiple occasions, and a thermal treatment was carried out to transform the porous $NiCo_2O_4$ nanobelt arrays via a process of calcination [55].

3.7. Combustion method

Combustion synthesis, also known as self-propagating high-temperature synthesis, is a highly versatile, assured, suitable, cost-efficient, and expeditious approach for the fabrication of nanomaterials. It encompasses a thermally tempted redox reaction between an organic fuel and a salt precursor acting as an oxidizing agent. Organic fuels such as citric acid, sucrose, and urea, among others, are commonly used. As the temperature increases from room temperature, the homogeneously mixed solution generates a significant amount of water vapor. Subsequently, when the mixed solution in the beaker is heat treated in the oven, it transforms into sol formation, sticky gel formation, and solid gel formation. Once the solid gel is acquired, the combustion of the gel can take place. This vigorous combustion can lead to the origination of a carbonous black fluffy mass, accompanied by the release of H_2O, CO_2, and N_2 gases. Liquid phase combustion synthesis, in comparison with solid-state, has proven to be the most qualified approach as the oxidizers and fuel can be dissolved readily in alcoholic or aqueous solution. The fine powders of $NiCo_2O_4$ are attained after the combustion is complete. Then, the powders are referred to as the as-prepared sucrose precursors. In the end, the precursors are subjected to calcination under an air atmosphere, resulting in the formation of $NiCo_2O_4$ nanoparticles. The complete combustion reaction is typically represented as follows (Fig. 9) [56]:

$$Ni(NO_3)_2 + 2Co(NO_3)_2 + C_{12}H_{22}O_{11} + 5O_2 \leftrightarrow NiCo_2O_4 + 12CO_2 + 11H_2O + 3N_2 \quad (3)$$

The nickel nitrate hexahydrate and cobaltous nitrate hexahydrate were dissolved in water separately and subsequently combined under agitation in stoichiometric proportions. Nitric acid was then added to the resulting mixture and stirred until a homogeneous clear solution was achieved. Citric acid, serving as the fuel, was introduced to the aforementioned mixture. In this case, a fuel-rich stoichiometric portion was deliberately selected to ensure the production of a phase-pure product. The resulting solution was mixed and heated until a gel-like solution appeared. Subsequently, the reaction vessel was transported to a preheated hot plate to eliminate any remaining water and initiate the combustion reaction. After a brief period, self-combustion occurred as the citric acid decomposed, releasing a significant amount of gas and heat. To examine the effect of crystallinity on the characteristics of $NiCo_2O_4$, calcinations were conducted by subjecting the as-prepared sample to heat [57].

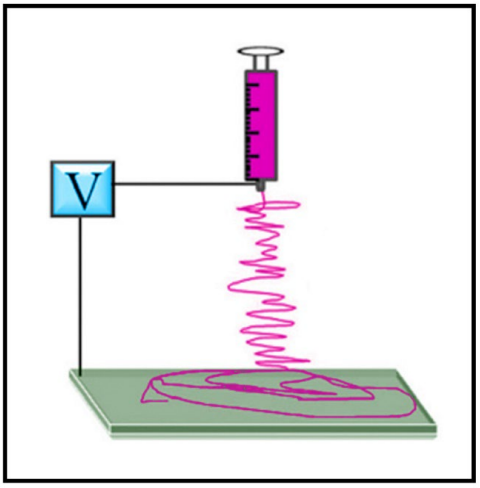

Fig. 7. Schematic diagram for preparation of $NiCo_2O_4$ by electrospinning method.

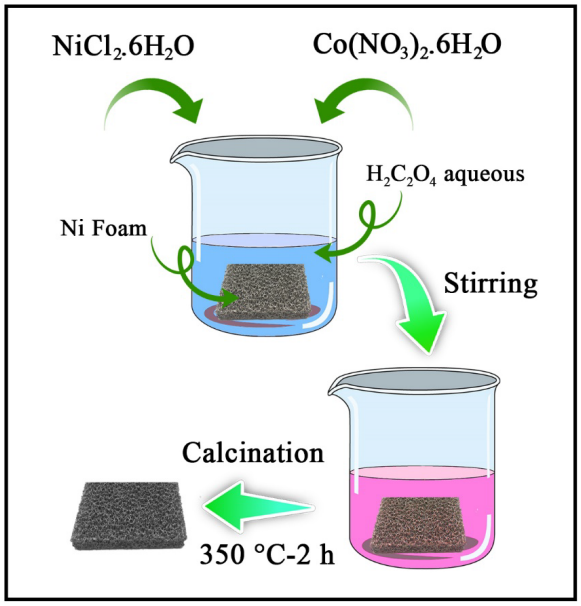

Fig. 8. Schematic illustrations of co-precipitation method for fabrication $NiCo_2O_4$.

While the combustion method presents an expeditious and cost-effective approach to synthesizing $NiCo_2O_4$ powders, this method does encounter significant limitations. These limitations include a lack of precise domination over both homogeneousness morphology and size of the particle, the immediate emergence of various crystal phases, the formation of vastly aggregated structures, a convoluted and undefined growth mechanism, and, crucially, a limited probability of producing a diverse and extensive array of morphological structures comparable to those obtained through hydrothermal and other solution approaches.

3.8. Microwave-assisted method

Microwaves refer to electromagnetic radiations characterized by a range of frequency spanning from 300 MHz to 300 GHz, accompanied by a wavelength variety of 1 mm to 1 m. The microwave-assisted method of synthesizing micro/nanostructures surpasses the traditional approaches mentioned previously due to its requirement of a significantly shorter reaction period, energy-saving, cost-efficiency, and ability to produce highly porous materials. Microwaves facilitate volumetric heating by penetrating through the entirety of the reactants. Diverse forms of polarization within the media containing space charge, directional, atomic, and electron polarization cause the induction of this volumetric heating in the direction of achieving superior morphological outcomes, the microwave-assisted approach for synthesizing nanomaterials is commonly joined with other techniques for example hydro/solvothermal, co-precipitation, sol-gel methods, among others. Recent studies have investigated the enhancement of the hydrothermal method through the incorporation of microwave assistance to synthesize $NiCo_2O_4$ micro/nanostructures. Alternative approaches to manipulate the structural features of $NiCo_2O_4$ involve the utilization of templates, ionic and organic solvents, capping agents, and suitable additives for growth [24].

In a typical experimental procedure as shown in Fig. 10, $Co(NO_3)_2$ and $Ni(NO_3)_2$ were became a solution in isopropanol and glycerol added. Subsequently, the mixture was vigorously stirred. The resulting mixture was then transferred into a vessel and, within a microwave hydrothermal reactor, subjected to microwave solvothermal treatment. To prevent any abnormal pressure increases caused by hot sites throughout the microwave heating process, a ramping procedure was employed to gradually elevate the room temperature. In the end, the sediment was washed away via deionized water and ethanol, after collection, and then dried, and annealed in an air environment with a temperature ramping [58].

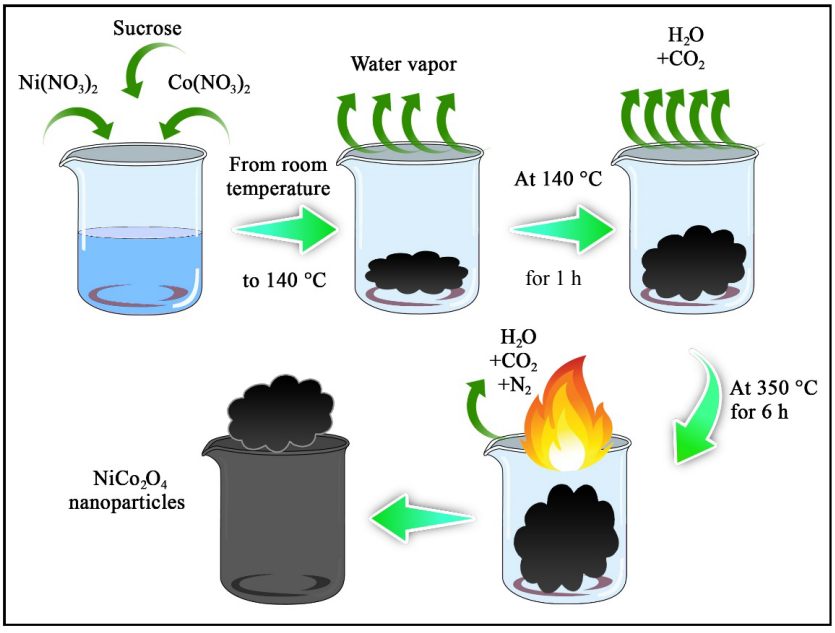

Fig. 9. Graphical representation of combustion method for the preparation of $NiCo_2O_4$.

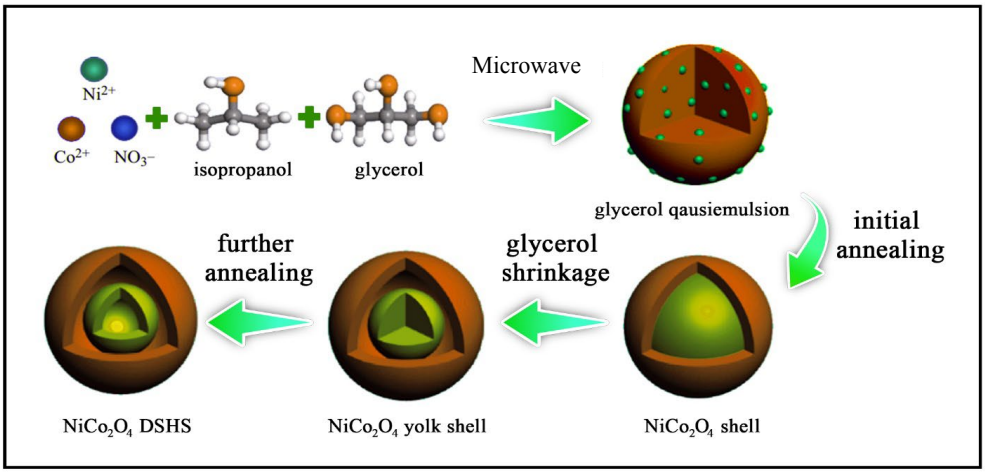

Fig. 10. Schematic illustration of the microwave-assisted procedure for the synthesis of $NiCo_2O_4$.

3.9. Spray pyrolysis method

In the technique known as spray pyrolysis, an aerosol consisting of several precursor constituents is equipped with a solvent deemed suitable and subsequently sprayed onto the substrate. Following this step, the solvent undergoes sequential evaporation from the substrate's surface, resulting in the precipitation of the solute. Afterward, high-temperature annealing takes place, leading to the formation of microporous particles. Finally, the solid particles undergo sintering. Various morphologies of $NiCo_2O_4$ nanostructures have been reported, including hollow nanospheres [24], hollow microspheres [59], plum-like particles [59], and yolk-shell microspheres[60].

In summary, nickel nitrate $Ni(NO_3)_2.6H_2O$ and cobalt nitrate $Cu(NO_3)_2.6H_2O$ were dissolved in de-ionized water in the appropriate ratio to create precursor solutions. These solutions were then subjected to filtration by a filter paper of Whatman, a process that was repeated three times. Subsequently, the resulting precursor solution was introduced into the ultrasonic generator. Upon activation of the ultrasonic generator, it produces minute aerosol droplets, which are subsequently directed into a silica reactor. To regulate the flow rate, two flask pumps were employed. The temperature within the silicon reactor was kept utilizing a tube furnace. Once the entire aerosol generation process was completed, both the furnace and the ultrasonic generator were cooled naturally to room temperature. The obtained products were then accessible from the pyrolysis collection chamber [61].

4. Comparison of synthesis methods

Each method has its own set of advantages and disadvantages. This study aims to evaluate the impact of different formation methods on the morphology and electrochemical performance of $NiCo_2O_4$ while keeping all other variables constant. The results indicate that the sol-gel method produced a higher specific capacity, while co-precipitation exhibited excellent rate performance. Both sol-gel and co-precipitation processes can yield porous, pure, and homogeneous structures like nanoparticles, whereas the hydrothermal method allows for the creation of well-defined morphologies by adjusting preparative parameters. The hydrothermal process is an effective way to synthesize nanostructured $NiCo_2O_4$-based materials with superior electrochemical performance by adjusting temperature parameters, surfactant types, and concentrations. The template method, which is environmentally friendly and renewable, can be used to fabricate highly ordered $NiCo_2O_4$ electrode materials with unique morphologies. Electrospinning is commonly used to produce fibers within a specific diameter range. Electrodeposition offers advantages in depositing $NiCo_2O_4$ onto conductive substrates and combining it with other high-performance materials for synergistic effects, which can be controlled by adjusting solution concentration and pH levels as well as applying overpotential. Table 1 provides a comparison of recent advancements in the specific capacity and stability of $NiCo_2O_4$-based electrodes with different morphologies synthesized using various methods.

Table 1. Comparison of the specific capacity of $NiCo_2O_4$ based electrodes.

Preparation method	Morphology	Specific capacity	Current density	Stability	Ref.
Template	Sub-microsphere	540 $F.g^{-1}$	10 $A.g^{-1}$	87% for 3500 cycles	[18]
Sol-gel	Nanoparticle	1080 $F.g^{-1}$	1 $A.g^{-1}$	94.8% for 100 cycles	[26]
Sol-gel	Spinel nanoparticles	1254 $F.g^{-1}$	2 $A.g^{-1}$	139.6% for 300 cycles	[28]
Sol-gel	Crystals submicron	217 $F.g^{-1}$	1 $mA.cm^{-2}$	96.3% for 600 cycles	[29]
Sol-gel	Submicron	217 $F.g^{-1}$	1 $mA.cm^{-2}$	96.3% for 600 cycles	[29]

Table 1. Continued.

Preparation method	Morphology	Specific capacity	Current density	Stability	Ref.
Sol-gel	Thin film	2157 $F.g^{-1}$	0.133 $mA.cm^{-2}$	96.5% for 10000 cycle	[30]
Sol-gel	Porous	1128 $F.g^{-1}$	5 $mA.cm^{-2}$	92.5% for 1000 cycles	[32]
Hydrothermal	Tremella-like	353.4 $F.g^{-1}$	10 $A.g^{-1}$	1000 cycles	[35]
Hydrothermal	Urchin-like	366.8 $F.g^{-1}$	10 $A.g^{-1}$	1000 cycles	[35]
Microwave-assisted hydrothermal annealing	Nanocrystals	215 $F.g^{-1}$	5 $mA.cm^{-2}$	-	[36]
Hydrothermal	Nanowires	1284 $F.g^{-1}$	2 $A.g^{-1}$	97.5% for 3000 cycles	[38]
Solvothermal	3D flower-like	1609 $F.g^{-1}$	1 $A.g^{-1}$	85% for 1000 cycles	[41]
Template	3D porous structure	871 $F.g^{-1}$	4 $A.g^{-1}$	80% for 2500 cycles	[49]
Electro deposition	Microspheres	188 $F.g^{-1}$	0.1 $A.g^{-1}$	95.1% for 1000 cycles	[50]
Electro deposition	Nanosheets	1590 $F.g^{-1}$	1 $A.g^{-1}$	85% for 5000 cycles	[51]
Electrospinning	Nanotubes	1647 $F.g^{-1}$	1 $A.g^{-1}$	93.6% for 3500 cycles	[52]
Co-precipitation	Porous	726.8 $F.g^{-1}$	1 $A.g^{-1}$	72.7% for 2000 cycles	[54]
Combustion	Nanostructure	903 $F.g^{-1}$	1 $A.g^{-1}$	90% for 1000 cycles	[57]
Spray pyrolysis	Hollow microspheres	902 $F.g^{-1}$	1 $A.g^{-1}$	89.2% for 2500 cycles	[59]
Spray pyrolysis	Hollow nanospheres	1007 $F.g^{-1}$	5 $A.g^{-1}$	78.7% for 3000 cycles	[61]
Sol-gel	Nano crystals	1860 $F.g^{-1}$	1 $A.g^{-1}$	75% for 1500 cycles	[62]
Co-precipitation	Nanostructure	1860 $F.g^{-1}$	1 $A.g^{-1}$	75% for 1500 cycles	[62]
Aerogels epoxide-driven sol-gel	Spinel nanoparticles	1400 $F.g^{-1}$	25 $mV.s^{-1}$	91% for 2000 cycles	[63]
Hydrothermal	Microrods	1671 $F.g^{-1}$	1 $A.g^{-1}$	-	[64]
Hydrothermal	Urchin-like	1348 $F.g^{-1}$	15 $A.g^{-1}$	90.8% for 2000 cycles	[66]
Solvothermal	Nanorods	90 $F.g^{-1}$	0.5 $A.g^{-1}$	94% for 2000 cycles	[66]
Template	Nanowire	1348 $F.g^{-1}$	10 $A.g^{-1}$	91.76% for 5000 cycles	[67]
Hard-template method (bi-solvent)	3D porous structure	658 $F.g^{-1}$	28.6 $A.g^{-1}$	95% for 2500 cycles	[68]
Bi-solvent	3D porous structure	739 $F.g^{-1}$	2.89 $A.g^{-1}$	95% for 2500 cycles	[68]
Electrochemical deposition	Microrod arrays	367 $F.g^{-1}$	47 $F.g^{-1}$	96% for 1500 cycles	[69]
Co-precipitation	Nanostructure	671 $F.g^{-1}$	1 $A.g^{-1}$	98% for 7000 cycles	[70]
Microwave-assisted	Flower shaped	1006 $F.g^{-1}$	1 $A.g^{-1}$	93.2% for 1000 cycles	[71]
Solution	1D nano-needle	1118 $F.g^{-1}$	5.56 $mA.cm^{-2}$	89.4% for 2000 cycles	[72]
Solution	Nanosheets	1743.4 $F.g^{-1}$	8 $mA.cm^{-2}$	93.3% for 3000 cycles	[73]
Solution	Nanowires	401 $F.g^{-1}$	1 $A.g^{-1}$	90% for 5000 cycles	[74]

5. Conclusions

Generally, supercapacitors exhibit a broad spectrum of potential applications in the field of energy storage. Herein, diverse methodologies employed for synthesizing spinel $NiCo_2O_4$ micro/nanostructures that possess versatile morphologies are provided. Furthermore, the subsequent utilization of these structures in developing supercapacitors is comprehensively explored. This review notably underscores the merits of $NiCo_2O_4$ as a material for supercapacitors, including its exceptional capacity for rapid charging, high energy storage capability, impressive power output, and outstanding long-term stability. Additionally, we propose rational enhancements to the electrochemical performance of $NiCo_2O_4$-based electrodes.

CRediT authorship contribution statement

Yalda Tarpoudi Baheri: Writing – original draft, Writing – review & editing, Supervision.
Amir Mahdi Homayounfard: Writing – original draft.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

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