Chapter

Supercapacitor Supported by Nickel, Cobalt and Conducting Polymer Based Materials: Design Techniques and Current Advancement

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Abstract

The recent advanced electronic appliances demand special high power devices with lightweight, flexible, inexpensive, and environment friendly in nature. In addition, for many industrial and automotive applications, we need energy storage systems that can store energy in a short time and deliver an intense pulse of energy for long duration. Till date the Li-ion battery is the only choice for fulfilling all our energy storage demands. However, the high cost, limited availability and non-environmental nature of electrodes and electrolyte material of Li-ion battery limits its applicability. Hence, the world demands an alternative replacement for the Li-ion battery. In this regard, the supercapacitor is one of the most emerging and potential energy storage devices. The electrode plays an important role in super-capacitors. The nickel and cobalt based oxide, hydroxides, and their composites with conducting polymer are promising and highly appreciated electrode materials for supercapacitors. This chapter covers the recent advances in supercapacitors supported by nickel, cobalt and conducting polymer based materials and their applications predominantly described in the recent literature. Recent advances are reviewed including new methods of synthesis, nanostructuring, and self-assembly using surfactant and modifiers. This chapter also covered the applications of supercapacitors in powering the light weight, flexible and wearable electronics.

Keywords: supercapacitors, mixed ternary metal oxides, nanostructured, $NiCo_2O_4$, energy density, etc.

1. Introduction

Supercapacitor (SCp) is also known as ultracapacitor. SCP is the advanced electrochemical energy storage device. At present, the lithium ion battery (LiBs), lead acid battery and SCP are the major available energy storage systems. Over the other energy storage systems, the SCP is stands out to be a promising energy storage device with very attractive properties such as high specific capacitance, high power density, moderate energy density, good cyclic stability, low cost, environmental friendly nature, etc. SCP has been utilized in various electrical applications viz.

hybrid vehicles, power backup, military services, and portable electronic devices like laptops, mobile phones, roll-up displays, electronic papers, etc. [1–3].

The performance of SCP is strongly depends on types electrode materials i.e. active material used in supercapacitor. Based on the type of active material used and process energy storage, the SCP can be divided into three main categories, including pseudocapacitors (PCs), electric double-layer capacitors (EDLCs) and hybrid capacitors [4–6]. In PCs metal oxides, metal hydroxides and conducting polymers are employed as active material. On the other hand, carbon base materials such carbon nanotubes, graphene and carbon black, etc. are used as active material in EDLCs employed. Likewise, the used of combination of metal oxide, conducting polymer and carbon based material as active material results hybrid capacitor. The PCs delivered high specific capacitance, high energy density than EDLCs, but demonstrates poor power density and cycle stability. Nevertheless, owing to the high active surface area, the EDLCs delivered high specific capacitance but suffer poor energy density than PCs [4]. The hybrid capacitors retain the advantage of both PCs and EDLCs and hence they delivered high specific capacitance, high energy density, and large cycle life [7, 8]. Moreover, the performance of supercapacitors is equally rely on different aspect of active material viz. quality, electric conductivity, material, size, porosity, synthesis method, etc. More specifically, the synthesis method can bring many attractive advantages in active material for extraordinary electrochemical performance of supercapacitor. Therefore, synthesis of active materials with high porosity, stable performance and good electrical conductivity has a very wide research potential.

Recently, to enhance the energy density, cycle life and electrochemical performance of the supercapacitors, the use of electrode material with desired structure with uniform porosity is one of the appealing strategies. From many decades, the nanostructured single transition metal oxides such as RuO_2 [9], MnO_2 [10], CeO_2 [11], Fe_2O_3 [12], Fe_3O_4 [13], Co_3O_4,, Mn_3O_4,, etc., and the nanostructured mixed ternary metal oxide (TMOs) such as $ZnFe_2O_4$, $NiFe_2O_4$ $CuFe_2O_4$, $CoFe_2O_4$, $MnCo_2O_4$ $ZnCo_2O_4$, $NiCo_2O_4$, and etc., and conducting polymers such as, polyaniline (PANi), polypyrrole (Ppy), polythiophene (Pth), etc. has been extensively used as active material for all types of supercapacitors. Out of the different materials used as the electrodes for SCp applications. The TMOs are highly studied and excessively used as active material in all types of supercapacitors. The mixed TMOs are also called the spinel metal oxide. The spinel TMOs have the general formula AB_2O_4. In AB_2O_4, the cubic crystal structure of TMOs consists of closely packed O^{2-} anions and an octahedral and tetrahedral space of the lattice occupied by the transition metal cations A and B, respectively. Due to this closed packed structure, the mixed TMOs show the extraordinary characteristics over single metal oxides, such as two order higher electrical conductivity, superior electrochemical performance and excellent stability over single metal oxides. Moreover, the recent research reports shows the TMOs have better structural advantages and higher surface area and porosity [14]. More specifically, the TMOs show low cost, natural abundance, low toxicity and environmental friendly nature. Hence, TMOs have drowned more research attention in recent years. In addition, the extraordinary electrochemical performance of TMOs in solid as well liquid electrolyte makes it a promising and potential candidate as electrode material for PCs. The various mixed TMOs viz. $ZnFe_2O_4$, $NiFe_2O_4$ $CuFe_2O_4$, $CoFe_2O_4$, $MnCo_2O_4$ $ZnCo_2O_4$, $NiCo_2O_4$, etc. has been utilized as electrode material for PCs. Out of the different TMOs the nickel and cobalt based TMOs have gained more research attention as electrode material in supercapacitors due to their attracting properties such as low cost, natural abundance, low toxicity and environmental friendly nature. More specifically, these materials show variable structures, diverse morphologies, high specific surface and uniform porosity and outstanding electrical conductivity. The $NiCo_2O_4$ demonstrated high electrical conductivity due to the presence of Ni in it. Whereas, Co enhances the electrochemical activity of oxides, further, the synergistic effect among Ni in Co offers high electrical conductivity with an excellent electrochemical behavior in supercapacitors [12]. The $NiCo_2O_4$ demonstrated a high theoretical capacity [15]. The nickel and cobalt based TMOs show diverse morphologies, this includes various nanostructures ranging from 0 to 3 D architectures viz. quantum dots, nanowires, nanosheets, platelets like nanoparticles, porous network like framework, coral- like porous crystals, ordered mesoporous particles, urchin-like microstructures and urchin-like nanostructures. Till date many recent attractive reviews have presented recent development in mixed TMOs as electrode material for SCs [7, 16–19]. We recommend few of them for readers who are new to this field of energy research.

In the present chapter we provide the recent advancements in synthesis of nanostructured nickel and cobalt base mixed TMOs and their composites with conducting polymer based materials as electrode material for supercapacitors predominantly described in the recent literature. Moreover, here our special emphasis will be on new methods of synthesis, nanostructuring, and self-assembly using surfactant and modifiers. In addition, we provide a summary of structural and morphological advancements regarding the electrochemical properties of supercapacitors. Finally, we link our discussion to the recent applications in powering the light weight, flexible and wearable electronics real world applications.

2. Synthesis of nickel and cobalt base mixed TMOs

Compared to the micro sized the nanostructured cobalt and nickel based TMOs show higher specific capacitance and long cycle life. Therefore many recent research strategies have drowned to synthesized nanosize mixed cobalt and nickel based TMOs. The various synthesis methods for synthesis of nanostructured cobalt and nickel based mixed TMOs viz., hydrothermal method sol–gel, thermal evaporation method, chemical bath deposition, electrodeposition, oil/water interfacial self-assembly strategy, etc. have been extensively reported in literature. Hydrothermal method is one of the excessively adopted synthesis methods for hierarchical nanostructure synthesis. This method is cost effective, simple, and easy to scale-up at room temperature. This method is mostly used for fine tuning the morphology and controlling the size of nanostructures. Agglomeration of $NiCo_2O_4$ results in low electrical conductivity and decreases the specific capacitance and cycle life of SCp [20]. Therefore, to enhance the electrical conductivity the use of high surface area with high porosity conductive substrates are highly recommended. These substrates enhance the contact between electrode and electrolyte and allowed more electrolyte ions penetration in active material. The various conductive substrates such as textiles, sponges, carbon clothes, carbon fibers, conventional paper, cables, etc. are used as substrates to fabricate SCs. Such conductive substrates are advantageous for enhancing the electrochemical performance via providing short diffusion path, high electrical conductivity, ample electroactive sites [21]. In this regard, Yang *et al.* synthesized the nanoneedle arrays of on filter carbon paper substrate via facial hydrothermal synthesis method. For fabrication the filter carbon paper submerged into the precursor of $NiCo_2O_4$ followed by calcination in the Argon atmosphere in the range of 250-400°C for 2 hours. Using this approach they have reported urchin like and nanoneedle arrays and further adopted this nanostructure for SCp applications [20]. The synthesis parameters like reaction temperature reaction temperature and reaction time controls the structures. Further, the calcination temperature after synthesis plays crucial role in improving the surface morphology, specific surface area, porosity, etc. [22]. Siwatch *et al.* [22] have reported the formation of $NiCo_2O_4$ quantum dots via hydrothermal synthesis and studied the effect of synthesis parameters like reaction temperature and time, and calcination temperature on the morphology of $NiCo_2O_4$ quantum dots. Further, the highly porous flower-like structure of $NiCo_2O_4$ quantum dots obtained at the calcination temperature 300^o C is highly useful for SCp applications. Lu *et al.* reported the synthesis of mesoporous $NiCo_2O_4$ via reagents assisted hydrothermal method and studied the effect of reagent cetyltrimethylammonium bromide (CTAB) on morphology and electrochemical behavior of $NiCo_2O_4$ for SCp applications. Moreover, the reagent during synthesis enhanced the specific surface area and charge transport of $NiCo_2O_{4.}$ As a result, the cyclic stability, rate performance and specific capacitance of $NiCo_2O_4$ quantum dots based in asymmetric SCp found to be increased [23]. Binder used during the fabrication of electrode increase the electrode resistance which further decreases the electrochemical performance and cycle life of SCp. Therefore recently binder free fabrication approaches such as direct growth on conductive substrate is more popular. Furthermore, over the conventional substrates the direct growth on three dimensional (3D) conductive substrate offers many advantages such as shorten the diffusion path, healthy synergy between the active material and electrolyte, provides ample electroactive site, etc. which further help to enhance the electrochemical performance of SCp. For example, Yang *et al.* [24] directly grown $NiCo_2O_4$ on gelatin-based carbonenickel foam (3D) by facial hydrothermal method followed by calcination at 350°C for 2 hrs under an Argon atmosphere.

The morphology of $NiCo_2O_4$ is reported to be nanoflower-like. The fabricated 3D electrode provides fast ions and electrons transfer rate and enhances the electroactive surface area of the $NiCo_2O_4$ via forming a complex 3D network. In addition, the nickel foam as substrate adds the electric conductivity whereas the gelatin based carbon on the nickel foam provides high surface area for uniform growth of NiCo2O4 during synthesis. In our previous study, we have reported the synthesis of nanostructured $NiCo_2O_4$ via surfactant assisted hydrothermal method and studied the effect surfactant and reaction parameters on the morphology of nanostructured $NiCo_2O_4$. From this synthesis, we got two distinct morphologies viz. platelet-like and nanorod-like using surfactants TEA ethoxylate and polyethylene glycol (PEG), respectively. We further used this nanostructured $NiCo_2O_4$ for SCp applications [18].

In addition to the hydrothermal method, the combustion method is one of the simple and easy to scalable synthesis methods. Over the hydrothermal method the combustion method does not requires Teflon-lined stainless steel autoclaves and centrifuge for product washing, is less time consuming and provides high phase purities. This regard, Kumar *et al.* reported the growth of $NiCo_2O_4$ on conductive substrate nickel foam using combustion method. For the synthesis, honeycomb-like $NiCo_2O_4$ the nitrate and glycine used as oxidizer and fuel, respectively [6].

For enhancing the surface area and porosity and electrochemical activities of $NiCo_2O_4$, the formation of composites of $NiCo_2O_4$ with carbon based material is one of the appealing strategies, for example, $NiCo_2O_4$/CNT, $NiCo_2O_4$/MWCNT, $NiCo_2O_4$/graphene, $NiCo_2O_4$/reduced graphene oxides (r-GO), etc. demonstrated to be a potential candidates for SCp applications. Carbon base material viz. CNT, MWCNT, graphene, r-GO, etc. provide excellent flexibility, high specific surface areas, remarkable electrical conductivity, good thermal and chemical stability [5, 25–27]. For example, Li *et al.* [25]. reported the synthesis of $NiCo_2O_4$/CNT composites, and studied the structure formation of $NiCo_2O_4$ with and without surfactant for supercapacitive applications. The nanoflakes and nanocorn like morphology for $NiCo_2O_4$ is obtained by using surfactant sodium dodecyl sulfate. Pathak *et al.* synthesized $NiCo_2O_4$ and $NiCo_2O_4$@ MWCNT composite using facile hydrothermal method.

$NiCo_2O_4$@ MWCNT demonstrated superior electrochemical performance and demonstrated a good electrode for SCp applications. In addition, using density functional they reveal the enhanced density of states near the Fermi level and increased quantum capacitance of the $NiCo_2O_4$ @SWCNT is one of the important reasons for high specific capacitance, high power density and energy density [28]. The PCs use reversible fast faradaic reactions to store electrical charges, which allow them to achieve higher capacitance by at least one order of magnitude than those obtained by EDLCs. Materials sustaining such redox reactions on their surfaces include, for example, conducting polymers and transition metal oxides.

3. Applications of Ni and Co based metal oxides and their composites

3.1 Pseudocapacitor (PCs)

Recently, PCs received considerable attention due to the one order higher capacitance, higher volumetric capacitance, higher energy density and use of low cost and easily synthesized active material than EDLCs. [28–30]. For example, Eskandari *et al.*. fabricated $NiCo_2O_4$ and its composite with PANi and MWCNTs and reduced graphene oxide r-GO and studied their SCp performance in 3 M KOH. Out of the different composites the $NiCo_2O_4$/PANi demonstrated superior performance and exhibited specific capacitance of 1760 Fg^{-1} (900 F/g and 734 F/g for $NiCo_2O_4$/ MWCNTs and NiCo2O4/r-GO, respectively) at current density of 1 Ag^{-1}, respectively. The highest specific capacitance in $NiCo_2O_4$/PANi is due to supplementary conductive pathways provided by PANi and synergistic effect of the rooted pseudo-reaction. Moreover the composite $NiCo_2O_4$/MWCNTs shows stable cycle is life and demonstrated to be best retention over all other composites as 89% over 2000 charge discharge cycles. Composite $NiCo_2O_4$ /r-GO also exhibited good cycle performance and shows retention in specific capacitance of 87% over 2000 charge discharge cycles. In addition, the pristine $NiCo_2O_4$ shows higher retention than $NiCo_2O_4$/PANi, i.e. 70% and 73%, respectively. The highest cyclic stability in $NiCo_2O_4$/MWCNTs is due to the high electrical conductivity and high mechanical strength of MWCNTs. In fact, the good cyclic performance in $NiCo_2O_4$/r-GO is the results of higher electrical conductivity, high surface morphology and good mechanical strength than PANi and pristine $NiCo_2O_4$ [31] Moreover, the representative Ni and Co based material and their performance in PCs are summarized in **Table 1**.

3.2 Hybrid capacitors

Even if the Ni and Co based TMOs are advantageous for SCp applications, however, in the long cycling process the rapid degradation of $NiCo_2O_4$ electrode materials is the major obstacle among the commercialization of $NiCo_2O_4$ based SCp. By increasing the electrical conductivity of $NiCo_2O_4$ this hurdle can be minimized and the higher rate capabilities can be attained. Therefore, from the last two decades, researchers devoted more efforts to enhance the electrical conductivity of $NiCo_2O_4$, this includes fabrication of hybrid composite with other conducting electrode materials, viz. carbon based material (CNts, SWCNts, MWCNts, activated carbon, doped and undoped reduced graphene oxides, etc.), conducting polymers, etc. In addition, recent formation of composite of $NiCo_2O_4$ with other mixed TMOs has gain enormous attention. For example, Mary *et al.* reported the fabrication of $NiCo_2O_4$ and $ZnCo_2O_4$ composites and studied their morphology dependent electrochemical behavior for hybrid SCp applications. In addition, the hybrid SCp

Sr. No.	Material	Method of synthesis	Electrolyte	Voltage window (V)	Specific capacitance (Fg^{-1}) at current density-scan rate	Energy density $Whkg^{-1}$	Retention of capacitance at (current density) (cycle numbers)	Reference
1.	$NiCo_2O_4$	Hydrothermal	1 M Na_2SO_4	0–0.6 V	479/ 5 mVs^{-1}	21.3	87.21% (5000)	[30]
2.	$NiCo_2O_4$	Hydrothermal	1 M Na_2SO_4	0–0.4 V	320 0.1 mVs^{-1}	16.1	95.34%, (1000)	[32]
3.	$NiCo_2O_4$ /NiCo2S4	Molecular design	—	0.1–0.6 V	1296 1 Ag^{-1}	44.8	93.2% (6000) 10 Ag^{-1},	[1]
4.	$NiCo_2O_4$	Hydrothermal	3 M KOH	0.0–0.6 V	3143 2 mVs^{-1}	56	48% (5000) 10 Ag^{-1},	[33]
5.	$NiCo_2O_4$ @α-Co(OH)2 nanowires	Hydrothermal	2 M KOH	−0.2 -0.5 V	1298-1 Ag^{-1}	39.7	83% (5000) 2 Ag^{-1}	[34]
6.	Mesoporous $NiCo_2O_4$ nano-needles	Hydrothermal	—	0.0–0.5 V	1410 Fg^{-1}-1 Ag^{-1}		94.7% (3000) 20 Ag^{-1}	[35]
7.	$NiCo_2O_4$ nanosheets	Solvothermal	—	—	2690 Fg^{-1}	52.6	80.9% (3,000) 20 mA cm^{-2}.	[36]
8.	$NiCo_2O_4$ PANi	Hydrothermal and in-situ polymerization	6 M KOH	0–0.5 V	3108 1 mA·cm^{-2}.	77.57	96.1% (1000)	[37]
9.	$NiCo_2O_4$ nanoneedles	Hydrothermal via annealing approach	1 M KOH	0–0.7 V	1076 0.5 Ag^{-1}	30.5	14% (1000) 10 Ag^{-1}	[38]
10.	$NiCo_2O_4$ nanoneedles	Pulsed laser ablation	3 M KOH	0–0.6 V	1650 Fg^{-1} 1 Ag^{-1}	56.7	91.78%, (12,000) 10 Ag^{-1}	[39]

Table 1.
Overview of representative Ni and Co based material and their performance in PCs.

Sr.No.	Material	Method of synthesis	Electrolyte	Voltage window (V)	Specific capacitance (Fg^{-1}) at current density/ scan rate	Energy density $Whkg^{-1}$	Retention of capacitance (cycle numbers) at current density	Reference
1	$NiCo_2O_4$ CNT	Hydrothermal	2 M KOH	−0.1- 0.5	574.3 0.5 Ag^{-1}	—	111.5% (1000)	[25]
2	$NiCo_2O_4$ @MWCNT	Hydrothermal	0.5 M K_2SO_4	—	374 2 Ag^{-1}	95	74.85% (3000)	[28]
3	3D $NiCo_2O_4$ /MWCNT	Sol–gel	2 M KOH	0–0.5 V	1010 0.1 Ag^{-1}	37.7	83.4% (2000) 2 Ag^{-1}	[40]
4	Ordered Mesoporous Carbon/$NiCo_2O_4$	co-precipitation	6 mol· L^{-1} KOH	0–0.6 V	577.0 1 Ag^{-1}	—	92.7%. (2000) 2 Ag^{-1},	[41]
5	$NiCo_2O_4$- nanoporous carbon.	Chemical	1 M KOH	−0.2-0.6 V	89 0.1 - Ag^{-1}	28	85% (2000)	[42]
6	Mesoporous carbon - $NiCo_2O_4$	hydrothermal followed by calcination	3 M KOH	−0.45-0.45	204.28 1 - Ag^{-1}	5.75	90.35% (3000) 20 Ag^{-1}	[43]
7	Hallow bamboo-shaped $NiCo_2O_4$	Template	6 M KOH	0.0–0.6 V	680.1C g^{-1} 1 Ag^{-1}	59.82	99.7% (5000) 10 Ag^{-1}.	[44]
8.	rGO- $NiCo_2O_4$ quantum dots	Chemical	1 M Na2SO4	0.0–1.6 V	265 0.73 Ag^{-1}	47	69% (1000)	[45]
9.	Oxygen-vacancy-rich $NiCo_2O_4$/nitrogen-deficient graphitic carbon nitride hybrids	Chemical	6 M KOH	0.0–0.6 V	1998 2 Ag^{-1}	70.22	95.22% (5000)	[46]
10	$NiCo_2O_4$@Ppy/CC	Hydrothermal	2 M KOH	0.0–0.5 V	155.4 mAh g^{-1} 1 mA cm^{-1}	22.3	71% (8000) 10 mA cm^{-2}	[47]

Table 2.
Overview of representative Ni and Co based material and their performance hybrid supercapacitor.

Sr. No.	Material	Method of synthesis	Electrolyte	Voltage window (V)	Specific capacitance (Fg^{-1}) at current density/ scan rate	Energy density $Whkg^{-1}$	Retention of capacitance (cycle numbers) at current density	Reference
1	$NiCo_2O_4$/C composites // activated carbon (AC)	Hydrothermal	6 M KOH	0–1.4 V	995.2 10 Ag^{-1},	20.87	83.04% (5000) 100 mVs^{-1}	[20]
2	$NiCo_2O_4$ quantum dots // reduced graphene oxide (rGO)	Hydrothermal	1 M Na_2SO_4	0–2.4 V	362, 0.5 Ag^{-1}.	69.5	86% (1000)	[22]
3	$NiCo_2O_4$ //AC	Hydrothermal	—	0–0.5 V	153.2 (1 Ag^{-1}),	22.5	97.1% (1000) 1 Ag^{-1}	[23]
4	$NiCo_2O_4$/ gelatin-based carbonenickel foam // AC	Hydrothermal		0–0.5 V	1416 (1 Ag^{-1})	48.6	88.5% (10,000) 5 Ag^{-1}.	[24]
5	$NiCo_2O_4$@Ni foam// sugar-derived carbon (SC)	Combustion	6 M KOH	0–0.5 V	169, 1.5 Ag^{-1}	48	96.5% (3000)	[6]
6.	MWCNTs intermingled $NiCo_2O_4$// Cu_2WS_4	Hydrothermal	3 M KOH	0–0.5 V	116 mAh g^{-1}, 1 Ag^{-1}	87	~88%, (10,000)	[5]
7.	$NiCo_2O_4$ nanoparticles and nanowires	Hydrothermal and wet chemical	1 M Na_2SO_4	0–1.6 V	1066.03 Ag^{-1}	59.56	77% (5000) 6.66 Ag^{-1}	[48]
8	$NiCo_2O_4$- carbon nanofiber	—	2 M KOH	—	991.96 5 Ag^{-1}	37.23	97.02% (3000) 30 Ag^{-1}	[15]
9	$NiCo_2O_4$/ r-GO	Hydrothermal	1 M KOH	0.0–1.6 V	702 0.5 Ag^{-1}	—	92% (1000) 4 mA cm^{-1}	[49]
10	$NiCo_2O_4$/ rGO	Co-precipitation	1 M KOH	0.0–0.6 V	1380 1 Ag^{-1}	—	90% (1000) 5 Ag^{-1} after	[50]

Table 3.
Overview of representative Ni and Co based material and their performance asymmetric supercapacitor.

fabricated using the $NiCo_2O_4$ and $ZnCo_2O_4$ composite and nitrogen doped activated carbon. The high surface area and uniform porosity of activated carbon in hybrid SCp enhances the capacitance via enabling the more electrolyte ions into active material. Interestingly, $NiCo_2O_4$ @ $ZnCo_2O_4$ composite shows high specific capacitance of 236 C g^{-1} at a current density of 1 A g^{-1}. Moreover, the aforementioned hybrid SCp results in high energy density of 101.6 $Whkg^{-1}$ and high retention in capacitance at 78.5% over 12000 charge–discharge cycles. Moreover, the representative Ni and Co based material and their performance in hybrid SCp are summarized in **Table 2**.

3.3 Asymmetric capacitors

The symmetrical SCp limits their specific capacitance due to narrow potential windows. Moreover, the use of aqueous base liquid electrolyte in symmetrical SCp decreases the specific capacitance energy density and cycle life. To overcome such drawback the fabrication of SCp with two different kinds of active material based electrode is demonstrated to be an effective strategy. The SCp fabricated using two different electrodes is termed an asymmetric supercapacitor. In asymmetric SCp positive electrode is fabricated using metal oxide base material, while negative electrode is fabricated by carbon based material. The combination of different active materials in a single device with higher operating potential result in higher the specific capacitance and energy density [40]. However, aqueous-based symmetric supercapacitors suffer from narrow potential windows, due to the limitation of the water decomposition. Therefore, an effective way is to construct asymmetric supercapacitor, which consists of two kinds of electrode materials, for instance positive electrode having pseudocapacitive nature and negative electrode having electric double layer capacitance with higher operating potential, for obtaining higher energy density [19, 20]. In the case of positive electrode materials, transition metal oxide based nanoparticles, conducting polymers based materials have been widely utilized, which exhibits pseudocapacitance as well as reversible redox Faradaic reaction. As negative electrode materials, carbon based materials like carbon nanotubes (CNT), graphene oxide (GO), activated carbon, and mesoporous carbon materials displaying electric double layer capacitance have been used. Among the carbon allotropes, mesoporous carbons have been extensively used as negative electrode material due to its high surface area and good electrical conductivity. For more understanding the recent advancements in $NiCo_2O_4$ and their composites and their performance in asymmetric SCp are summarized in **Table 3**.

4. Conclusions and outlooks

With ever increasing energy demands, day by day the SCp gaining much interest as an energy storage device. From a many years, the nickel and cobalt based TMOs and their composites have been studied and successively employed as an active material in all types of SCp. The nanostructured $NiCo_2O_4$ is low cost, in abundance, environmentally friendly in nature and has high electrical conductivity. In addition, due to the enhanced mobility of charge carriers the nanostructured $NiCo_2O_4$ demonstrated to be higher electrochemical performance than the single metal oxides. In this regard, the recent advances in synthesis of pristine $NiCo_2O_4$ and their composites with diverse morphologies and their applications for electrochemical performance in all types of SCp have been summarized in this chapter. Out of the different synthesized methods used for synthesis nanostructured $NiCo_2O_4$, the hydrothermal method is found to be excessively used. Moreover, the hydrothermal method is demonstrated to be more advantageous for the synthesis of diverse morphologies ranging from 0 D to 3 D, and resulted in high specific surface area and uniform porosity. The pristine nanostructured $NiCo_2O_4$ has many limitations for its commercial supercapacitor applications. Therefore, advanced strategies like synthesis of hierarchical nanostructures of $NiCo_2O_4$ and the fabrication of composite with other mixed TMOs, carbon based material and conducting polymers can enhance the specific capacitance, energy density and rate capability of Ni and Co based supercapacitors.

Conflict of interest

The authors declare no conflict of interest.

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