

Chapter 9

Transition Metal Oxides as Supercapacitor Materials

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9.1 Introduction

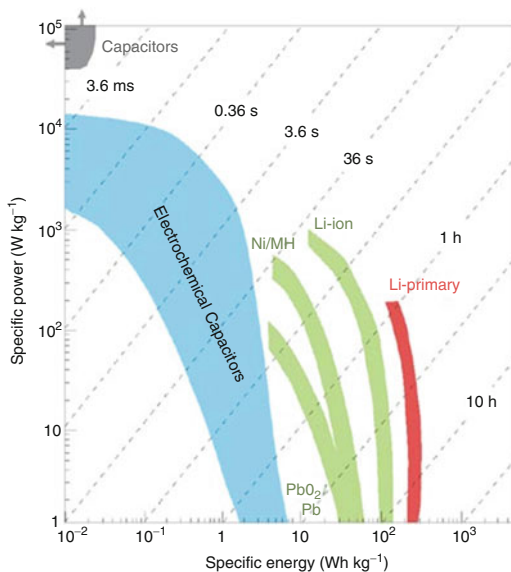
The rapidly growing commercial markets in electric vehicles and portable electronic products have created a seemingly insatiable demand for high-performance energy storage devices [1]. However, it seems hard to meet the increasingly higher standards by using the current energy conversion or storage devices alone, such as lithium-ion batteries or fuel cells. Supercapacitors (SCs), also called electrochemical capacitors, store charges through either ion adsorption/desorption (electrochemical double-layer capacitors, EDLCs) or fast surface redox reactions (pseudocapacitors), which can complement or replace batteries in electrical energy storage when high-power delivery or uptake is needed [2]. According to charge storage mechanisms, SCs may be placed into two distinctive classes: EDLCs and pseudocapacitors [3]. As is well known, SCs have the advantages of high power density, ultralong cycle life, and rapid recharge capability, devoting to meeting the ever-growing consumption demands and alleviating the energy crisis [4, 5]. The Ragone plot [2] in Fig. 9.1 (power density against energy density) shows that SCs shorten the gap between conventional capacitors and batteries.

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Fig. 9.1 Ragone plot (specific power against specific energy) for various electrical energy storage devices (Reprinted from Ref. [2] with permission. Copyright 2008, Macmillan Publishers Limited)



SCs were first reported in 1957 Becker's patent [6] and then emerged in the commercial market in 1978 (gold capacitors from Panasonic/Matsushita) and 1980 (supercap from NEC Tokin) [7]. Generally, they can serve as load-leveling and uninterruptible power supplies, such as backup sources for memories and microcomputers, and have great potential applications in electric vehicles or hybrid electric vehicles. Since the 1990s, electrochemical capacitors ushered in its development with materials used as EDLCs mainly based on carbonaceous materials such as activated carbon [8, 9], carbon nanotube [10, 11], and graphene [12–14] which provide large surface areas for electrical charges to reside. Alternatively, pseudocapacitors utilizing transition metal oxides and conductive polymers combine electrosorption with fast surface redox reactions to store energy, where the amount of charge held is proportional to the applied voltage [7]. Researchers had no clear concept regarding pseudocapacitance until Trasatti and Buzzanca discovered the capacitive properties of RuO_2 [15].

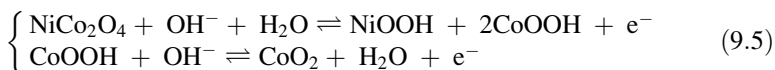
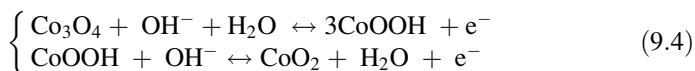
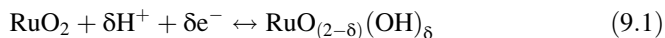
Note that electrode materials have become the core competence for supercapacitors and could be typically divided into three types including carbon materials, conducting polymers, and transition metal oxides. Carbon materials with low cost, extremely developed surface area (up to $3000 \text{ m}^2 \text{ g}^{-1}$), and good electrical conductivity and chemical stability seem to be ideal materials for electrochemical double-layer capacitors, but it usually suffers from low specific capacitance (commonly lower than 400 F g^{-1}) [16–18]. While conducting polymers have higher specific capacitance (usually lower than 530 F g^{-1}) and excellent intrinsic conductivity, however, their cycle life is extremely poor because of substantial expansion and contraction during the charging–discharging process [19, 20]. Compared with these two types mentioned above, transition metal oxides usually possess multiple oxidation states that are in favor of fast redox reaction resulting in a much higher specific capacitance [21]. Impressively, specific capacitance of pseudocapacitors

obtained from conducting polymers and transition metal oxides can be 10–100 times higher than EDLCs obtained from carbon materials [22].

While supercapacitors benefit from the large power capability (as high as 10 kW kg^{-1}), high current capability, ease of maintenance, and long-term cycling stability ($> 10^6$ cycles) [23], their moderate energy density for the widespread deployment in everyday technology using clean and renewable energy media is still far away to meet the performances and cost requirements, in particular providing power boosts to start the engine or to assist acceleration. In order to make capacitors commercially viable and extensively used, the energy that they can store needs to increase significantly and to endow supercapacitors with sufficient energy for higher requirements in the future is still a challenge. Extensive efforts have been devoted to improving the specific capacitance of supercapacitors by introducing pseudocapacitive metal oxides. In this way, cheap transition metal oxides with high energy density are very attractive electrode materials for supercapacitors to realize commercialization quickly.

9.2 Energy Storage Mechanism

Transition metal oxides store its charges both on the surface and in the bulk near the surface of the solid electrode where the electrochemical processes occur. Moreover, it should be noted that the metal oxides possess not only double-layer capacitance but also high pseudocapacitance (typically $10^{\sim}100$ times higher than double-layer capacitance), whereas the double-layer capacitances shown by CV curves for the electrodes are relatively too small to be observed [24]. In general, two kinds of electrolytes including alkaline solution and acid solution are used to analyze their corresponding electrochemical performances. Typically, RuO_2 and MnO_2 electrodes are measured in H_2SO_4 solution, while NiO , Co_3O_4 , and NiCo_2O_4 use KOH as electrolyte, thus obtaining remarkable pseudocapacitances; their pseudocapacitive behaviors in the electrolyte can be described by the following equations [24, 25]:



As typical pseudocapacitor electrode materials, ruthenium oxides have a completely different mechanism with that of electrochemical double-layer

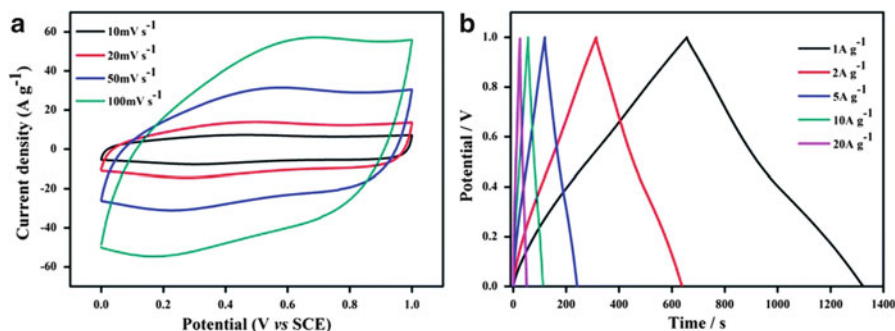
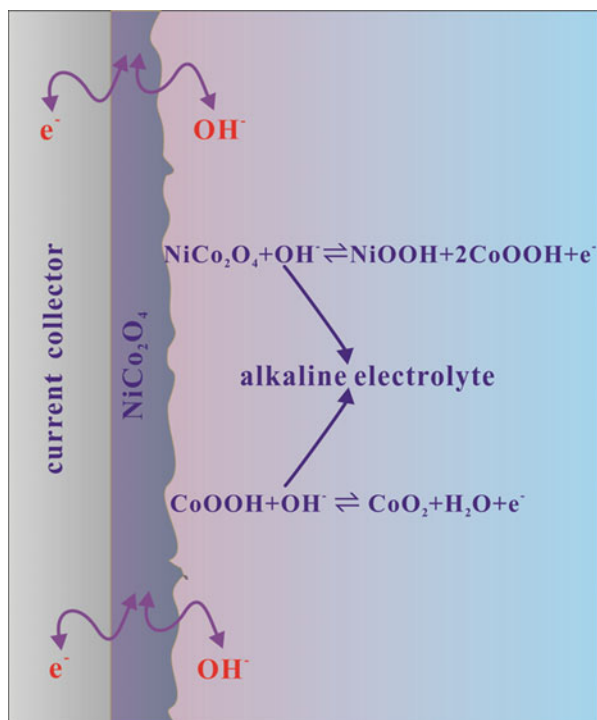


Fig. 9.2 (a) The cyclic voltammetry (CV) curve and (b) galvanostatic charge–discharge curve of RuO_2 (Reprinted from Ref. [29] with permission. Copyright 2014, The Royal Society of Chemistry)

capacitors and possess multiple redox states and good electrical conductivity. RuO_2 has three distinct oxidation states accessible within 1.2 V, and its pseudocapacitive behavior in acidic solutions can be described by Eq. (9.1). Protons can participate in the redox reaction, where RuO_2 acts as a proton condenser and the reaction is electrochemically reversible. Amorphous structures are the key parameter in determining the value of specific capacitances, as the proton can be easily intercalated into the bulk of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ but not into the crystalline phase [26, 27]. It is also proposed that hydrous ruthenium dioxide has an improved capacitive properties, better than those observed from anhydrous structures, as hydrous regions are more permeable to protons and proton conduction inside ruthenium dioxide is dominant when compared with the electron conduction [28]. The cyclic voltammetry (CV) curve and galvanostatic charge–discharge curve [29] are displayed in Fig. 9.2a and b. It shows a nearly rectangular shape and good coulombic efficiency as high as $\sim 100\%$, which is closely related to the superlong cycle life and excellent rate capacity.

Very recently, spinel NiCo_2O_4 has sparked worldwide concern as an attractive pseudocapacitive electrode material for supercapacitor application due to its many intrinsic advantages. It possesses a ferrimagnetic cubic spinel structure with multiple redox states and good electrical conductivity as a P-type semiconductor with the band gap of 2.1 eV [30]. Note that NiCo_2O_4 adopts a spinel structure in which all the nickel cations occupy the octahedral interstices, whereas the cobalt cations are distributing among the tetrahedral and octahedral interstices [31]. The redox reactions offered by nickel cobaltite, including contributions from both nickel and cobalt ions, are richer than those of the monometallic nickel oxides and cobalt oxides as illustrated in Eq. (9.5). In addition, the electrical conductivity of nickel cobaltite is at least two orders of magnitude higher than that of pure Co_3O_4 and NiO , which facilitates to acquire better cycling performance and fast charge–discharge capability [32, 33]. It is noteworthy that, in the charging–discharging process (Fig. 9.3), there exist valence state changes of $\text{Co}^{3+}/\text{Co}^{4+}$ as well as $\text{M}^{2+}/\text{M}^{3+}$ ($\text{M} = \text{Co}$ or Ni) on the surface of the electrode materials, where

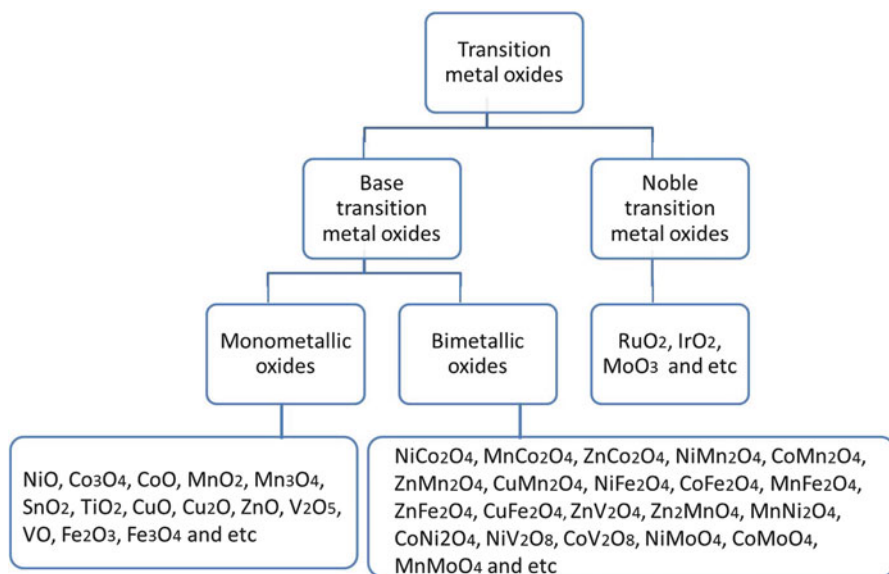
Fig. 9.3 Schematic of charge storage mechanism for supercapacitors based on NiCo_2O_4 (Reprinted from Ref. [24] with permission. Copyright 2014, The Royal Society of Chemistry)



fast and reversible faradaic reactions occur [33, 34]. The electrochemical redox potentials of $\text{M}^{2+}/\text{M}^{3+}$ and $\text{Co}^{3+}/\text{Co}^{4+}$ transitions are so close that the redox peaks observed overlap as one. Intriguingly, the specific capacitance of NiCo_2O_4 is observed to rise after several hundred cycles in some work which attributed to their unique morphologies and process of activation (potential cycling). Other transition metal oxides have the same storage mechanism and are not covered here.

9.3 Transition Metal Oxides for Supercapacitors

Transition metal oxides as the basis for supercapacitors can be typically divided into two types: noble metal oxides and base transition metal oxides. Noble metal oxides include RuO_2 , IrO_2 , etc., while base transition metal oxides for supercapacitors are developing from monometallic oxides (such as NiO , Co_3O_4 , Fe_3O_4 , and Mn_3O_4) to single-phase bimetallic oxides (such as NiCo_2O_4 , MnCo_2O_4 , NiMoO_4 , NiFe_2O_4 , and CoMn_2O_4). The supercapacitor materials based on transition metal oxides are summarized and classified in Scheme 9.1.



Scheme 9.1 Classification of transition metal oxides utilised as supercapacitor materials

9.3.1 Noble Metal Oxides

Nanostructured materials facilitate to help ameliorate the electrochemical performances of transition metal oxides, taking advantage of revealing the essentials during the charge–discharge process and grasping the key element in fabricating nanomaterials by transforming bulk transition metal oxides into nano-porous structures. Noble metal oxides such as RuO_2 , IrO_2 and so forth were first found exhibiting good capacitive properties with remarkable electrochemical performances. In 1971, Trasatti and Buzzanca first reported that RuO_2 films could form a rectangular shaped cyclic voltammogram which closely resembled the carbon-based electrochemical double-layer capacitor [15]. Since this pioneering report, researchers have explored the capacitive properties of RuO_2 extensively since its theoretical value of specific capacitance could be as high as $1300 - 2200 \text{ F g}^{-1}$ [35]. RuO_2 is a rare stoichiometric oxide which possesses wide potential window, remarkably high specific capacitance, high rate capability, long cycle life, thermal and chemical stability, and metallic-type conductivity [36]. The key methodology to boost the specific capacitance is their morphological and chemical composition design, as high surface-to-volume ratio with suitable pore sizes is desirable for the penetration of electrolytes and reactants into the whole electrode matrix and can promote the electrochemical double-layer capacitances and provide a large amount of superficial electroactive species for faradaic redox reactions. More specifically, the factors playing key roles in the electrochemical behavior of Ru oxides mainly

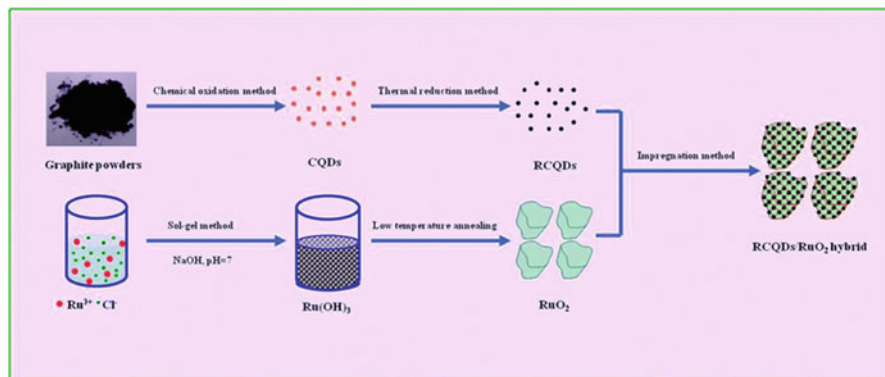


Fig. 9.4 Preparation procedure for the RCQD/RuO₂ hybrid (Reprinted from Ref. [40] with permission. Copyright 2013, The Royal Society of Chemistry)

include specific surface area, the combined water in RuO_x, the crystallinity of RuO₂, the size of RuO₂·xH₂O, and electrolytes used [37].

Generally, there are two common methods to prepare ruthenium oxides for supercapacitor applications. One is the chemical vapor deposition that synthesizes nanomaterials by thermal decomposition and then oxidization of the precursor at high temperatures [38, 39]. The other is the sol–gel method which firstly produces a sol–gel of precursor followed by annealing at low temperatures. It was reported that amorphous ruthenium oxides obtained at low temperatures of 150 °C show specific capacitance as high as 720 F g⁻¹, while in the crystalline phase annealing with temperature beyond 175 °C exhibited rapidly dropped specific capacitance [26].

Recently, it was reported that the group of Ji et al. developed a sol–gel method fabricating carbon spheres at RuO₂ [29] and carbon quantum dots at RuO₂ [40] hybrid for supercapacitors, demonstrating ultrahigh rate capability and excellent cycling stability. The excellent electrochemical performance was mainly attributed to the formation of the hybrid structure, which facilitates the fast charge transportation and ionic motion during the charge–discharge process and greatly improves the utilization of RuO₂, leading to rapid redox reactions. The process of fabricating carbon quantum dots at RuO₂ is elaborated in Fig. 9.4. In addition, Zhang et al. synthesized nanotubular ruthenium oxides by using manganite nanorods as a morphology sacrificial template and obtained a high specific capacitance of 860 F g⁻¹ with a good capacitive retention [41]. Extensive research has been undertaken by researchers in this field with the specific capacitance reported to reach more than 1300 F g⁻¹. For example, Hu et al. [35] used the membrane-templated synthesis route to obtain hydrous RuO₂ (RuO₂·xH₂O) nanotubular structures by means of an anodic deposition technique. The obtained ruthenium oxide exhibited an ultrahigh specific capacitance of 1300 F g⁻¹, excellent charge–discharge behavior at 1000 mV s⁻¹, and high-frequency (4.0–7.8 kHz) capacitive responses, which were much higher than any value ever reported before.

Iridium dioxide with its rutile structure is also a transition metal oxide for supercapacitors applications. In comparison with RuO_2 , the fact that IrO_2 did not draw much attention for supercapacitor applications can mostly be owing to its relatively small value of specific capacitance [42]. For example, Chen et al. fabricated a composite of IrO_2 and multiwalled carbon nanotubes, which showed a low specific capacitance of 69 F/g [43]. This was then extended to IrO_x nanofoils with high surface area and then sputtered upon on multiwalled carbon nanotubes for supercapacitor application, exhibiting an improved specific capacitance of 370 F g^{-1} , which is still poor when compared with RuO_2 [42].

9.3.2 Base Transition Metal Oxides

9.3.2.1 Monometallic Oxides

NiO

NiO is a very versatile material and has shown to exhibit good electrochemical activity based on the transformation process of NiO/NiOOH. Various morphologies such as flowers [44], hollow spheres [45, 46], and nanosheets [47] have been successfully prepared by different methodologies.

A number of chemical methods have been used to prepare nanostructured nickel oxides such as chemical precipitation, chemical bath deposition, microwave route, sol-gel process, and hydrothermal method [25]. In traditional chemical precipitation methods, Ni(OH)_2 precursor is first obtained by adding precipitants into a soluble nickel salt such as $\text{Ni(CH}_3\text{COO)}_2$ and $\text{Ni(NO}_3)_2$, and then Ni(OH)_2 is calcinated into NiO at high temperatures. The preparation method is facile, low cost, and suitable for large-scale production of NiO. For example, Zhang et al. [48] reported a facile hydrothermal process to grow various porous NiO nanostructures including nanoslices, nanoplates, and nanocolumns by calcinating β - Ni(OH)_2 . Consequently, the samples exhibited specific capacitances of 176, 285, and 390 F g^{-1} at a discharge current of 5 A g^{-1} , respectively.

Sol-gel process is another efficient way to obtain desired nanostructures. Typically, the first step is to prepare a sol-gel and the second step is to apply heat treatment. The sol-gel process seems very simple; however, in fact it is difficult to control. As reported, Yang et al. [49] obtained hexagonal and single crystalline NiO nanowires by a sol-gel process followed by calcination. In addition, NiO_x xerogels were formed by a sol-gel method followed by annealing at 250 °C, obtaining a maximum specific capacitance of 696 F g^{-1} [50].

There are some other methods such as chemical bath deposition [51], hydrothermal methods [52], and microwave routes [53] that are widely used in preparing NiO for supercapacitor applications. Nickel oxide is considered as an alternative electrode material for SC in alkaline electrolytes due to the advantages of high

specific capacitance (theoretical specific capacitance of 3750 F g^{-1}), environment friendliness, and low cost; however, it faces the challenges involving poor cycle performance and high resistivity [37]. The cycle performance and conductivity of nickel oxide could be improved by introducing cobalt ions into the nickel oxide matrix or combining with carbon materials [54, 55].

MnO₂

Manganese oxide (MnO₂) is advantageous to its low cost, no toxicity, easy accessibility, and large energy density and consequently has been considered as one of the most promising materials in application of SCs. MnO₂ has not only a larger energy density but also is more economical than noble transition metal oxides. Over the past years, significant efforts have been directed toward the synthesis of nanomaterials with controlled sizes and ordered morphologies owing to the close relationship between the morphology and the capacitive performances.

The most common method to prepare MnO₂ is a hydrothermal synthesis in which Mn²⁺ is often used as raw material, and the as-prepared mixture solution is placed in a Teflon-lined pressure vessel. It has been demonstrated that the morphology of MnO₂ depends much on the dwell time of hydrothermal process, showing an evolution of crystallinity of the nanostructures as the hydrothermal dwell time increased from 1 to 18 h. Scanning electron microscopy (SEM) images of nanostructure MnO₂ exhibiting different morphologies are depicted in Fig. 9.5, and the MnO₂ nanostructures prepared at 140 °C for 6 h showed the best performance [56]. Electrochemical deposition is another effective methodology to prepare nanostructured MnO₂. For example, Tao et al. [57] have successfully prepared a solid-state supercapacitor based on a PPy – MnO₂ nanoflake-carbon fiber hybrid structure by electrochemical deposition process. The device exhibited a high-volume capacitance of 69.3 F cm^{-3} at 0.1 A cm^{-3} and a large energy density of $6.16 \times 10^{-3} \text{ Wh cm}^{-3}$ at 0.04 W m^{-3} . Furthermore Li et al. [58] developed an electrospinning approach to fulfill scale and thickness requirements of nanostructured MnO₂ electrodes. The MnO₂ electrode for supercapacitors could also be fabricated by a sol–gel method. For instance, Pang et al. [59] fabricated an MnO₂ film via dip coating or drop coating with manganese dioxide suspensions (sols) onto nickel foils, showing high specific capacitance of 698 F g^{-1} .

Regarding MnO₂ as SC materials, several challenges should be addressed, including partial dissolution problem of MnO₂ in the acidic electrolyte and its poor electronic conductivity and ionic conductivity. Impressively, Kang et al. [60] improved the electronic conductivity of MnO₂ by nonequilibrium Au doping changing the electronic structure of MnO₂, demonstrating a high specific capacitance (626 F g^{-1} at 5 mV s^{-1}) and excellent cycling stability (7 % increment after 15,000 cycles). Furthermore, Zhang et al. [61] investigated the electrochemical properties of MnO₂ in 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim] PF₆)/N,N-dimethylformamide (DMF) electrolyte, fabricating a

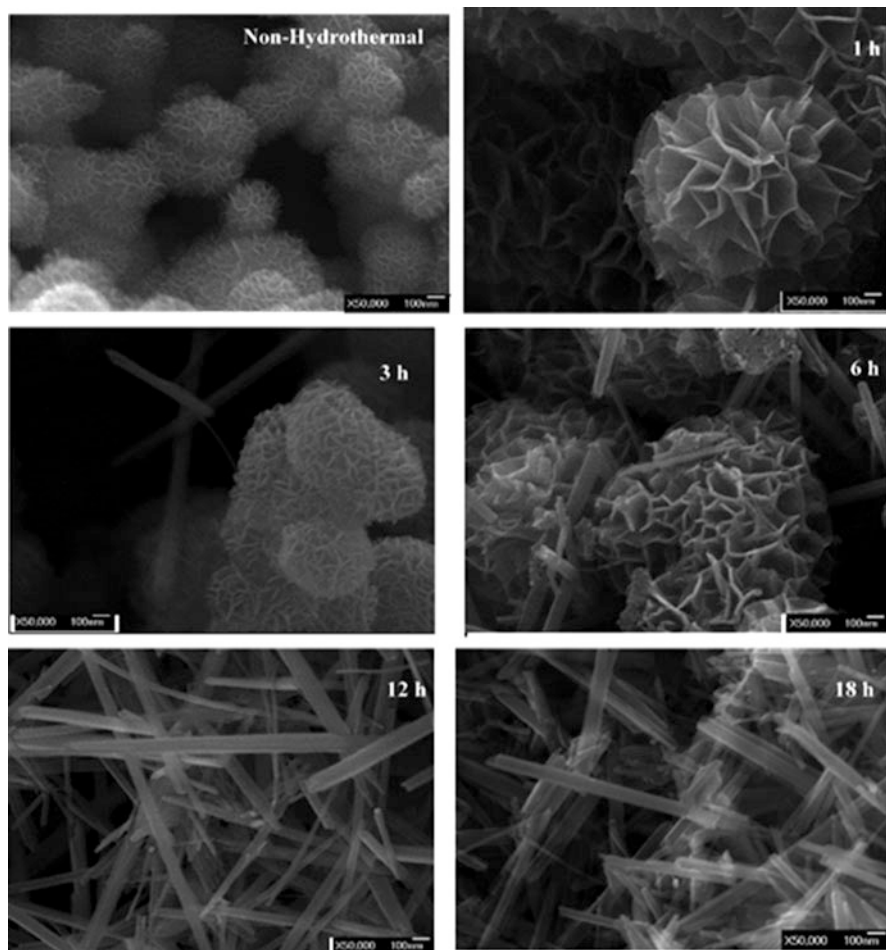


Fig. 9.5 SEM images of MnO₂ prepared at different hydrothermal dwell times (Reprinted from Ref. [56] with permission. Copyright 2005, American Chemical Society)

high-voltage (3 V) asymmetric supercapacitor with a maximum specific energy of 67.5 Wh kg⁻¹ and a maximum specific power of 20.4 kW kg⁻¹. The impressive results revealed that [Bmim] PF₆/DMF can be a promising electrolyte for MnO₂-based supercapacitors.

Extensive work is ongoing to prepare a better modality of MnO₂ achieving higher specific capacitances, and the whole electrochemical performances of asymmetric supercapacitors have also been improved by enhancing the electrochemical properties of the negative electrode and the voltage of the whole cell.

Co₃O₄

Co₃O₄ is an important transition metal oxide for supercapacitors with excellent reversible redox behavior, high conductivity, and good stability. Different methods have been performed to synthesize Co₃O₄ nanostructures with morphologies from one dimension to three dimensions. In general, these methodologies consist of two steps: formation of precursor and calcination. Great efforts have been made to improve the electrochemical performance of Co₃O₄ by constructing different morphologies and combining with other novel materials.

For example, Co₃O₄ nanocrystals with well-controlled shapes, including nanosheets and microspheres assembled from nanosheets, have been successfully prepared by a facile ethanolamine-directed solvothermal method and sequential thermal decomposition at atmospheric pressure [62]. Moreover, Xia et al. [63] developed a facile hydrothermal synthesis method to prepare self-supported hollow Co₃O₄ nanowire arrays on various conductive substrates, revealing high specific capacitances with 599 F g⁻¹ at 2 A g⁻¹ and 439 F g⁻¹ at 40 A g⁻¹, thus making it suitable for high-rate supercapacitor applications. The enhanced capacitive performance is due to its unique porous structure and hollow structure which could provide fast ion and electron transfer, good strain accommodation, and large reaction surface area. Chen et al. [64] reported a simple hydrothermal method through in situ growing Co₃O₄ nanowires on three-dimensional graphene foam grown by chemical vapor deposition, demonstrating high specific capacitance of ~ 1100 F g⁻¹ at a current density of 10 A g⁻¹ with remarkable cycling stability. These recent studies indicate that appropriate morphology, microstructure, and chemical composition are important in achieving high-performance SC based on Co₃O₄.

9.3.2.2 Bimetallic Oxides

NiCo₂O₄

Nickel cobaltite (NiCo₂O₄) has become a new class of energy storage material for supercapacitors with outstanding electrochemical performance, delivering not only large power density but also high energy densities [65]. This material possesses richer electroactive sites and at least two magnitudes higher electrical conductivity than that of Co₃O₄ and NiO. Moreover, it shows comparable capacitive performances with noble metal oxides of RuO₂, but with much lower cost and more abundant resources. It is believed that the redox reactions offered by nickel cobaltite, including contributions from both nickel and cobalt ions, are richer than those of the monometallic nickel oxides and cobalt oxides. More importantly, multiple oxidation states and various nanostructures can also enable rich redox reactions for spinel nickel cobaltite to store more charges [32, 33, 66]. Last but not least, there are abundant nickel and cobalt elements on the earth, and it seems to be a promising

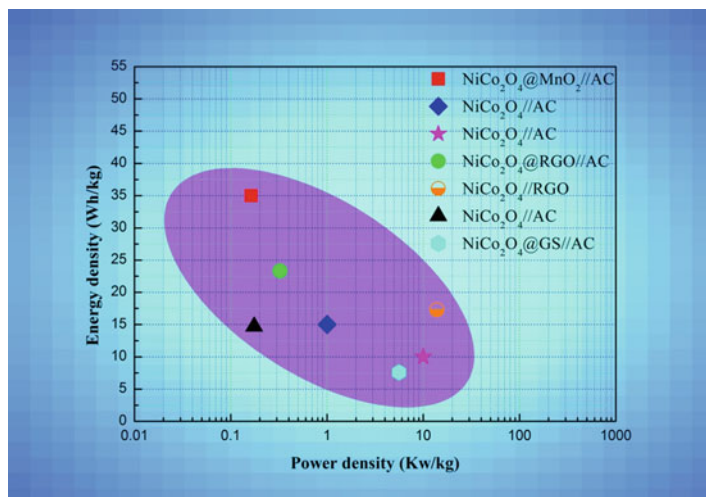


Fig. 9.6 Ragone plot of the current electrochemical performance for NiCo₂O₄-based asymmetric supercapacitors (Reprinted from Ref. [24] with permission. Copyright 2014, The Royal Society of Chemistry)

opportunity for nickel cobaltite to be widely applied and quickly industrialized as electrode material for supercapacitors due to its environmental friendliness and low cost [67]. To some extent, NiCo₂O₄ is playing an important role in complementing or replacing electrode materials based on Co₃O₄, NiO, and RuO₂ in energy storage field. A Ragone plot, as shown in Fig. 9.6, is derived from NiCo₂O₄-based asymmetrical supercapacitors' work which illustrates the performances in terms of energy density versus power density indicating this material is beneficial.

The methods for preparing NiCo₂O₄ for supercapacitors can primarily be divided into three categories: (i) sol–gel method, (ii) hydrothermal synthesis, and (iii) electrodeposition process. In brief, the synthetic route of NiCo₂O₄ nanomaterial can be thought as the formation of precursor followed by an annealing process. These three methods are summarized in Fig. 9.7 and are discussed in detail below; other pertinent methods are also briefly mentioned.

In general, the sol–gel method can be briefly defined as the conversion of a precursor solution into an inorganic solid by a chemical means [68]. Herein, the precursor solution consists of either an inorganic metal salt or a metal organic species, while nickel and cobalt acetates, halides, and nitrates are typically employed here for preparing NiCo₂O₄ [69, 70]. It is well known that the sol–gel method is simple and cheap with products of high purity, homogeneity, and porosity, mainly including four steps: (a) preparation of the precursor solutions, (b) formation of the intermediates as sol, (c) transformation from sol to gel, and (d) calcination at high temperature. Note that solvents, surfactants, reaction time, and temperature are crucial regulatory factors for obtaining appropriate structures with outstanding electrochemical performances [68].

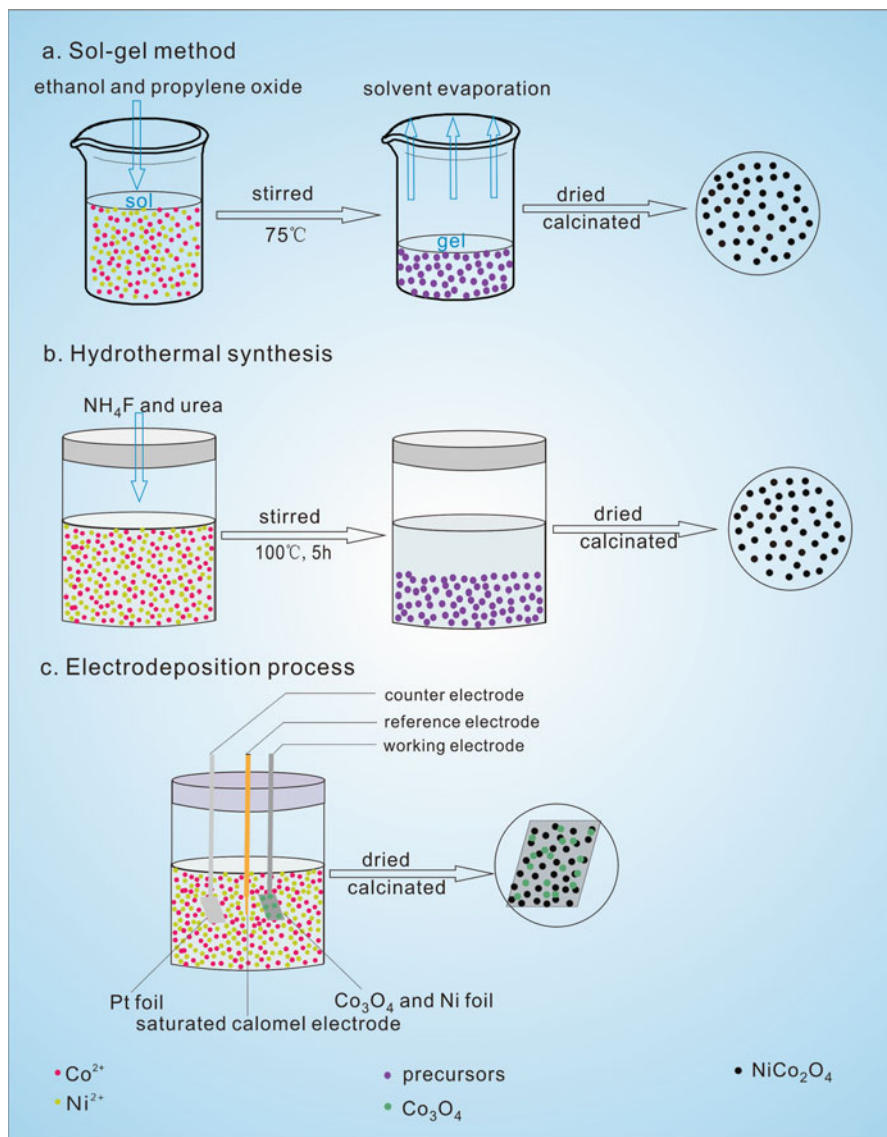
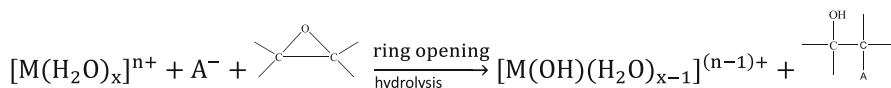


Fig. 9.7 Typical synthetic approaches of NiCo₂O₄ for supercapacitor application (Reprinted from Ref. [24] with permission. Copyright 2014, The Royal Society of Chemistry)

Hu and coworkers [71] first reported the preparation of NiCo₂O₄ aerogels via an epoxide-driven sol-gel process in 2010, which showed an ultrahigh specific capacitance of 1400 F g⁻¹ with a mass loading of 0.4 mg cm⁻². The majority of the pores were in the optimal sizes of 2–5 nm for supercapacitor applications, and the as-obtained aerogels were of excellent reversibility and cycle stability. Since this

pioneering work, several researches have been devoted to this sol–gel approach. The typical preparation process is illustrated in Fig. 9.7a, and the mechanism of gelation can be explained by the following reaction where M represents nickel or cobalt ions and where A^- denotes Cl^- or NO_3^- ions [72]:



Additionally, Kong et al. [73] developed a sol–gel process by adding different surfactants, such as hexadecyltrimethylammonium bromide (CTAB) and polyvinyl alcohol (PVA), to control the microstructure and surface morphology of $NiCo_2O_4$ nanoparticles. The product modified by CTAB displays the highest specific capacitance of 1440 F g^{-1} at a current density of 5 mA cm^{-2} , while Wu et al. [74] pointed out that the initial molar concentration of reactants, reaction time, and solvent species involved are crucial for preparing the target products. Through the use of citric acid as the chelating ligand and H_2O –DMF as solvent via a facile sol–gel process, the submicron-sized $NiCo_2O_4$ particles exhibited a specific capacitance of 217 F g^{-1} with high mass loading of 5.6 mg cm^{-2} . Recently, Ji et al. [75] discussed the effect of three different chelating agents including citric acid, oxalic acid, and ethylenediaminetetraacetic acid on fabricating spinel $NiCo_2O_4$ via a facile sol–gel method, revealing that $NiCo_2O_4$ prepared by oxalic acid has the highest specific capacitance of 1254 F g^{-1} at 2 A g^{-1} due to the relatively higher specific surface area, while $NiCo_2O_4$ prepared by ethylenediaminetetraacetic acid exhibits the best rate capability and cycling stability owing to the relatively larger pore size. Extensive work is being carried out via sol–gel processes to prepare a better modality of $NiCo_2O_4$ so as to achieve a higher specific capacitance and a longer cycle life. It has been proven to be an effective way indeed to synthesize $NiCo_2O_4$ electrode materials with low cost and high electrochemical performances.

Hydrothermal/solvothermal synthesis refers to the heterogeneous chemical reactions in a sealed heated solution to dissolve and recrystallize materials above ambient temperature and pressure conditions [76]. Hydrothermal synthesis and solvothermal synthesis are similar synthetic strategies that are distinct from whether the solution is aqueous or not. For convenience and habit, we call this hydrothermal synthesis. In general, the precursors of $NiCo_2O_4$ are formed by a combination of reaction substances being heated in a sealed Teflon-lined stainless steel autoclave. As the most common method of synthesizing nickel cobaltite, hydrothermal method is advantageous to form highly monodispersed nanoparticles with a control over size and morphology.

A large number of groups have made attempts to optimize the reaction conditions and form special morphologies so as to enhance the electrochemical performances of $NiCo_2O_4$ electrodes [77–84]. For example, Chen et al. [77] reported that a 3D hierarchical $NiCo_2O_4$ nanosheet–nanowire cluster arrays were manufactured via a facile hydrothermal method, exhibiting an ultrahigh specific capacitance of 2000 F g^{-1} at 10 A g^{-1} with 93.8 % retention (more than 10,000 cycles) and a high

power density of 26.1 kW kg^{-1} at a current density of 80 A g^{-1} . As illustrated in Fig. 9.7b, the process is based on Ni–Co nitrates induced by NH_4F and urea being heated in a sealed Teflon-lined stainless steel autoclave at 100°C for 5 h. Zou et al. [79] also reported a facile hydrothermal method that successfully grew 3D NiCo_2O_4 microspheres constructed by radial chain-like NiCo_2O_4 nanowires with different exposed crystal planes, demonstrating high specific capacitance (1284 F g^{-1} at 2 A g^{-1}), good rate capability, and excellent cycling stability (only 2.5 % loss after 3000 cycles). It was proposed that the chain-like nanowires with different exposed crystal planes exhibited higher electronic conductivity than other mesoporous NiCo_2O_4 nanostructures. In comparison, solvothermal method just occurs in nonaqueous solvents such as ethanol and ethylene glycol. Very recently, the 3D flowerlike NiCo_2O_4 hierarchical architectures have been fabricated by An et al. [78] via a solvothermal method using polyvinylpyrrolidone (PVP) as the structure-directing agent in a polytetrafluoroethylene (PTFE) reaction environment followed by a simple thermal annealing treatment, displaying a large surface specific area of $212.6 \text{ m}^2\text{g}^{-1}$ and a high specific capacitance of 1191.2 F g^{-1} at current densities of 1 A g^{-1} ; however, it suffered from a relatively poor cycling performance due to the electric isolation caused by collapse of the nanosheets. Meanwhile, Ji et al. [84] successfully fabricated 3D network-like mesoporous NiCo_2O_4 nanostructures through a solvothermal route coupled with a post-annealing treatment. Benefiting from the large specific surface area ($170.6 \text{ m}^2\text{g}^{-1}$) and abundant mesoporosity (5–10 nm), the as-obtained NiCo_2O_4 manifests high specific capacitance of 931 F g^{-1} at 3 A g^{-1} .

The electrodeposition process occurs in the electrolysis of plating solutions where micron- or submicron-sized particles are suspended, and variable amounts of these particles are embedded in the electrochemically produced solid phase with special properties [85]. As illustrated in Fig. 9.7c, the process can be described in three steps: (1) formation of precursor solution, (2) co-electrodeposition of nanoparticles, and (3) thermal decomposition. Due to cooperative formation mechanism of the composite electrode, as a general rule, ultrahigh specific capacitances and good cycling performances will be achieved through this novel method.

For instance, Du et al. [86] electrodeposited NiCo_2O_4 nanosheet arrays onto flexible carbon fabric successfully, which displayed high specific capacitance of 2658 F g^{-1} (2 A g^{-1}), good rate property, and superior cycling life. Note that carbon fabric (CF) is an ideal conductive substrate for directly growing active materials owing to its superior electrical conductivity, good flexibility, and high mechanical strength, through which we can fabricate some distinctive flexible supercapacitors or lithium-ion batteries. Moreover, Lou and his coworkers [87] reported the synthesis involving the co-electrodeposition of a bimetallic (Ni, Co) hydroxide precursor on an Ni foam and subsequently thermal transformation to spinel mesoporous NiCo_2O_4 , and the electrode exhibited an ultrahigh specific capacitance of 1450 F g^{-1} even at a very high current density of 20 A g^{-1} . The sizes of interparticle mesopores ranged from 2 to 5 nm, which were important indeed to facilitate the mass transport of electrolytes within the electrodes for fast redox

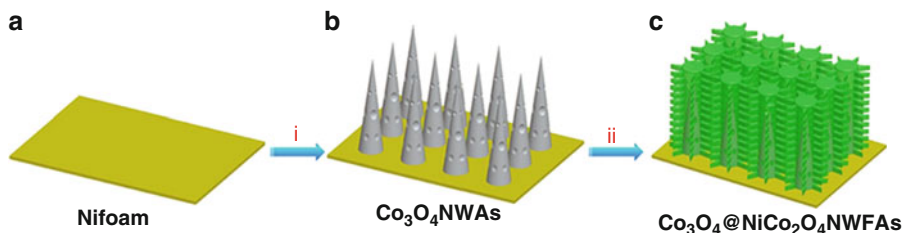


Fig. 9.8 Illustration of the formation process of $\text{Co}_3\text{O}_4@\text{NiCo}_2\text{O}_4$ NWFA hierarchical heterostructures. (a) Ni foam substrate; (b) hydrothermal synthesis of aligned Co_3O_4 nanowire arrays; (c) formation of hierarchical $\text{Co}_3\text{O}_4@\text{NiCo}_2\text{O}_4$ nanoflake arrays via a co-electrodeposition process (Reprinted from Ref. [89] with permission. Copyright 2013, Elsevier Ltd)

reactions and double-layer charging–discharging. Composite electrodes such as $\text{Ni}(\text{OH})_2@\text{NiCo}_2\text{O}_4$ [88] and $\text{Co}_3\text{O}_4@\text{NiCo}_2\text{O}_4$ [89] via the electrodeposition method were also reported in the literature. And the formation process of the nanoforest of hierarchical $\text{Co}_3\text{O}_4@\text{NiCo}_2\text{O}_4$ [89] nanowire arrays is elaborated in Fig. 9.8 as a typical example.

The electrodeposition process is widely used to fabricate composite electrodes with different nanomaterials. It is very important to choose the befitting materials that should possess good electrical conductivity or unique nanostructure to assist the target material in pursuing for better electrochemical performances. However, the ambiguous relationship between the composite structures and electrochemical performances has not been clarified yet.

As elaborated above, all of the three major methods are distinctive. The sol–gel method tends to acquire nanoparticles of high purity, homogeneity, and porosity. And the hydrothermal synthesis is controllable of size and nanostructure by adjusting temperature parameters or types and concentration of auxiliaries. By contrast, the electrodeposition process has some distinct advantages in depositing NiCo_2O_4 onto various conductive substrates such as nickel foams and carbon textiles and combining NiCo_2O_4 with other excellent materials that show intriguing synergistic effect, which can be manipulated through adjusting solution concentration, solution pH value, and applied overpotential or current density in the electrodeposition procedure. In addition, other methods, such as coprecipitation method, template approach, and microwave technique, are also simply mentioned below, which are not widely used or just assistant measures for fabricating NiCo_2O_4 material, and the following examples are only constructed for the purpose of comprehensively illustrating the diversity and novelty of processes as reported.

Recently, coprecipitation method is getting popular owing to its simple and facile process [90–92]. For example, Ji et al. [92] reported a facile coprecipitation way using NaHCO_3 as precipitant, and the as-obtained uniform porous NiCo_2O_4 nanoparticles showed high specific capacitance of 726.8 F g^{-1} (1 A g^{-1}) and good cycle stability of 72.7 % retention at a current density of 5 A g^{-1} after 2000 cycles. In addition, it has been reported that microwave technique has been used to help prepare NiCo_2O_4 electrodes for supercapacitors. What is more, the

microwave-assisted process has been demonstrated to be advantageous to extremely fast kinetics of crystallization, very rapid heating to the required temperature, and possible formation of new metastable phases, which facilitate to tune the crystal size and phase transformation degree of binary Ni–Co precursors [93, 94]. As a flexible and efficient approach, the template approach, using silica spheres [95] and sodium dodecyl sulfate [96] as templates, has also been used to synthesize hierarchical mesoporous hollow NiCo_2O_4 sub-microspheres and hexagonal mesoporous NiCo_2O_4 for supercapacitor electrodes, respectively. Both of the electrodes show remarkable electrochemical performances. Besides, sonochemical precipitation technique [97], chemical bath deposition [98], reflux synthesis [99], room-temperature solid-state reaction [100], and single-spinneret electrospinning technique [101] have also been utilized to synthesize NiCo_2O_4 nanostructures for supercapacitors. These approaches deserve a mention and readers are directed to these for further details.

MnCo_2O_4

As a potential candidate for supercapacitors, spinel MnCo_2O_4 has been restricted by the poor ionic conductivity and partial dissolution in alkaline electrolytes [102]. Despite some disappointing physicochemical properties of MnCo_2O_4 , it is believed that MnCo_2O_4 -based supercapacitors can be modified by combining with certain carbonaceous materials which possess both light weight and good electronic conductivity [103]. It is fascinating that the faradaic redox reactions of MnCo_2O_4 occurring in the charge–discharge process are speculated to be both $\text{Co}^{2+}/\text{Co}^{3+}/\text{Co}^{4+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}/\text{Mn}^{4+}$, which facilitate to achieve much higher energy density with multiple valence changes [104].

As reported by Kong et al. [103], the spinel MnCo_2O_4 fabricated by a facile sol–gel method displayed high specific capacitance of 405 F g^{-1} at 5 mA cm^{-2} , remarkable rate capability of 67.9 % capacity retention at 40 mA cm^{-2} , and good cycle stability of 4.9 % loss after 1000 cycles, owing to the porous structure and fairly stable spinel structure. In addition, Li et al. [105] developed a new strategy to prepare a flowerlike $\text{C}@\text{MnCo}_2\text{O}_4$ hybrid composite using a facile hydrothermal method combined with a post-calcination process. Due to the unique hollow structure, high specific surface area, and suitable pore channels, the $\text{C}@\text{MnCo}_2\text{O}_4$ composite exhibits high specific capacitance, low charge transfer resistance, and superior capacitance retention. A high specific capacitance of 728.4 F g^{-1} has been achieved at a current density of 1 A g^{-1} , and 95.9 % of the initial capacitance is still retained after 1000 cycles. Recently, Xu et al. [106] successfully prepared porous MnCo_2O_4 nanowires by hydrothermal method followed by a calcinating process, showing excellent capacitance and desirable rate performance (1342 F g^{-1} at 1 A g^{-1} and 988 F g^{-1} at 20 A g^{-1}).

NiFe₂O₄

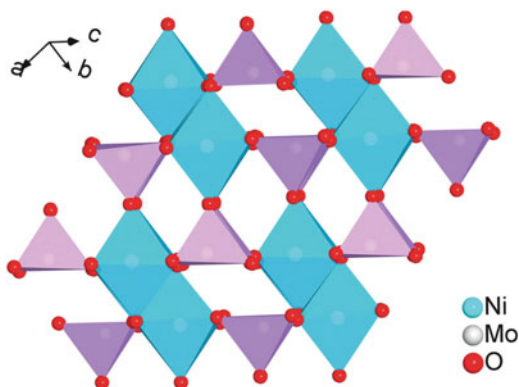
Spinel NiFe₂O₄ can be a promising candidate for use as supercapacitor materials due to its low cost and environmental friendliness. However, it exhibits low electrical conductivity, small energy density, and poor cycling performance.

For example, Wang et al. [107] reported a facile synthesis of RGO–NiFe₂O₄ composites by a hydrothermal process. The synthesized electrodes were measured in a 1 M Na₂SO₄ aqueous solution, showing the best capacitive properties of 459.6 F g⁻¹ at 1 A g⁻¹ due to the suitable particle size and good dispersion property of the active material. Senthilkumar et al. [108] reported the PANI–NiFe₂O₄ composites prepared by an in situ chemical oxidative polymerization method, which provided high specific capacitance of 448 F g⁻¹ and good capacitance retention of 80 % after 1000 cycles. In addition, Sen et al. [109] developed a sol–gel method to prepare nanocrystalline nickel ferrites (5–20 nm), exhibiting good electrochemical performance.

NiMoO₄

NiMoO₄ has drawn significant research attention because of its excellent electrical conductivity and outstanding electrochemical performance resulting from the high electrochemical activity of the Ni element and the good electrical conductivity of the Mo element [110]. The crystalline structure of NiMoO₄ is depicted in Fig. 9.9, and it displays that NiMoO₄ occupies the monoclinic structure with molybdenum atoms and nickel atoms adopting the tetrahedral and octahedral sites, respectively. Note that the edge-sharing NiO₆ octahedra interconnected by MoO₄ tetrahedra facilitate to constitute a 3D network structure with open channels, which are beneficial for ion diffusion [111]. Different morphologies of NiMoO₄, such as nanosheets [112, 113], nanorods [114], nanowires [115–117], and nanotubes [118], have been developed for pseudocapacitive application, and typical

Fig. 9.9 Crystal structure of NiMoO₄ (Reprinted from Ref. [111] with permission. Copyright 2014, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)



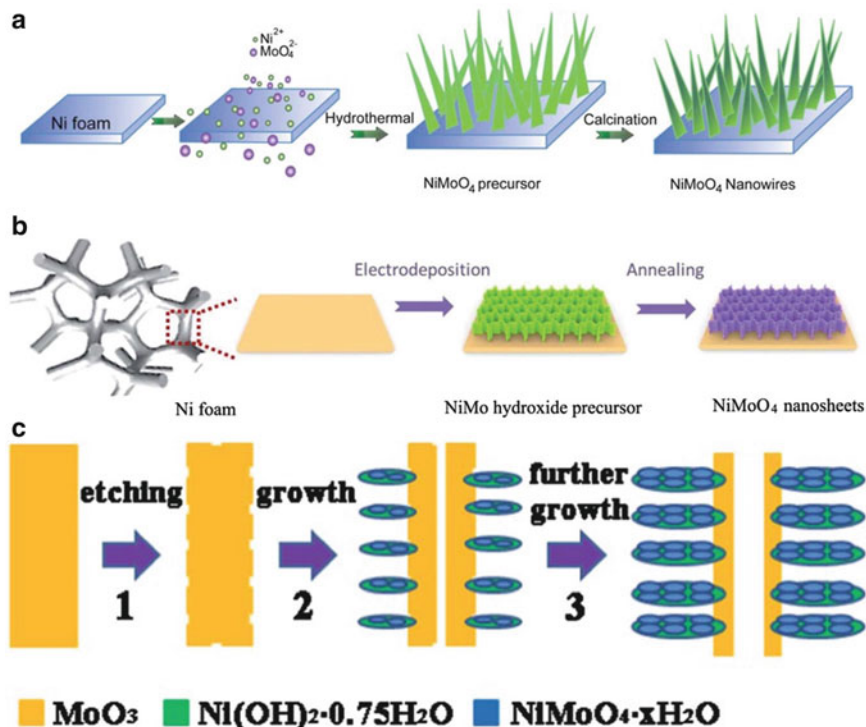


Fig. 9.10 Schematic illustration of the preparation process of NiMoO₄. (a) Hydrothermal method; (b) electrodeposition process; (c) hydrothermal method (Reprinted from Ref. [110] with permission. Copyright 2015, The Royal Society of Chemistry. Reprinted from Ref. [115] with permission. Copyright 2013, The Royal Society of Chemistry. Reprinted from Ref. [118] with permission. Copyright 2015, The Royal Society of Chemistry)

approaches [110, 115, 118] for synthesizing NiMoO₄ electrode materials are described in Fig. 9.10.

For example, Wang and his coworkers [110] have reported that amorphous honeycomb-like NiMoO₄ nanosheets can be prepared by electrodeposition process followed by thermal treatment. The as-prepared NiMoO₄ nanosheets with interconnecting pore channels and an ultrathin structure showed a high specific capacitance (1694 F g⁻¹ at 1 A g⁻¹ and 1220 F g⁻¹ at 50 A g⁻¹) and excellent cycle performance (92.7% after 9000 cycles). Peng et al. [111] developed a facile hydrothermal method to grow hierarchical NiMoO₄ architectures assembled from well-aligned nanosheets or nanorods on various conductive substrates for supercapacitor applications. It was found that NiMoO₄ nanosheets manifest higher specific capacitance and better cycling stability than NiMoO₄ nanorods and the assembled asymmetric supercapacitors based on NiMoO₄ nanosheets and activated carbon delivered a high energy density of 60.9 Wh kg⁻¹ at a power density of 850 W kg⁻¹. Wang and his coworkers [114] synthesized NiMoO₄ nanospheres by a

facile hydrothermal method, demonstrating high specific capacitance of 974.4 F g^{-1} at 1 A g^{-1} .

By virtue of the synergistic effect, the composite electrode based on NiMoO_4 has been extensively investigated. Composite electrodes for supercapacitors, including $\text{Co}_3\text{O}_4 @ \text{NiMoO}_4$ [119–121], $\text{MnO}_2 @ \text{NiMoO}_4$ [122], $\text{NiCo}_2\text{O}_4 @ \text{NiMoO}_4$ [123], $\text{Co}(\text{OH})_2 @ \text{NiMoO}_4$ [124], $\text{CoMoO}_4 @ \text{NiMoO}_4$ [125, 126], and $\text{graphene} @ \text{NiMoO}_4$ [117], have been reported recently. For example, Liu et al. [125] designed $\text{CoMoO}_4\text{--NiMoO}_4$ bundle composite material for supercapacitors by a chemical coprecipitation method, and the composite electrode showed a maximum specific capacitance of 1039 F g^{-1} at 2.5 mA cm^{-2} and an excellent rate capability ascribing to its unique microstructure, large specific surface area, multiple oxidation states, and synergistic effects between NiMoO_4 and CoMoO_4 . In addition, Zhang et al. [115] developed a 3D sea urchin-like $\text{NiCo}_2\text{O}_4 @ \text{NiMoO}_4$ core–shell structure constructed by interconnected ultrathin nanosheets via a facile two-step hydrothermal method using a post-annealing procedure. The $\text{NiCo}_2\text{O}_4 @ \text{NiMoO}_4$ material revealed a high specific capacitance of 2474 F g^{-1} at 1 A g^{-1} and 2080 F g^{-1} at 20 A g^{-1} and maintained 95.0 % of the initial capacitance after 1000 cycles at 10 A g^{-1} , which can be attributed to its unique 3D core–shell and hierarchical mesoporous structures.

Considering the promising electrochemical performance of NiMoO_4 and easy fabrication process, it can be one of the most potential electrode materials applied for supercapacitor in the future energy storage/conversion fields.

9.4 Summary and Outlook

Significant progress has clearly been made in electrochemical supercapacitors which has sparked worldwide attention due to the rapid development of supercapacitive electrode materials, which is of great significance to fast industrialize this important energy storage/conversion device. Since the first report of supercapacitors in 1957, electrode materials have developed from carbon materials to pseudocapacitive materials, while transition metal oxides for supercapacitors have developed from noble transition metal oxides to base transition metal oxides, from monometallic oxides to single-phase bimetallic oxides, and from mono-component materials to multicomponent composites. Note that bimetallic transition metal oxides usually have great advantage over monometallic transition oxides, including higher electrical conductivity, multiple valence changes, and potential synthetic effects. In addition, multicomponent composites such as transition metal oxides at carbon materials utilizing as supercapacitive electrode material have the advantages in obtaining more remarkable rate capability and much better cycle performance. It tends to combine the different virtues together, thus enhancing the electrochemical performances of supercapacitors.

Inspiringly, transition metal oxides have already been demonstrated to display striking performance as electrode materials for electrochemical supercapacitors. However, the majority of the reports regarding the applications of transition metal oxides for supercapacitors are still retained in the laboratory, with few solutions yet for a mass market. Most researches only focus on preparing various nanostructures for transition metal oxides, while little studies are devoted to improving the whole production process of the whole device of supercapacitor. Optimizing the manufacturing process and reducing the production cost are also vital to realize large-scale production for the industrial applications, and designing products based on market demand can more effectively and healthily promote the development of supercapacitor. Meanwhile, a comprehensive understanding of the relationship between the property/performance and the structure/composition of these transition metal oxides for supercapacitors should be systematically established. Developing reliable and efficient methods and criteria to solve this problem is urgently needed. The establishment of theoretical simulation and mathematical modeling is also highly anticipated to investigate the detailed energy storage mechanism and the rational design of electrode materials, directing the purposeful design of facile, low-cost, and large-scale preparation of transition metal oxides with excellent electrochemical performance.

At present, electrochemical supercapacitors based on transition metal oxides should provide improved energy density on the premise of keeping high power density. However, there is still considerable distance to meet the demand of commercial application. Narrow stable potential window of aqueous electrolytes greatly restricts the enhancement of energy density, and limited mechanism study cannot effectively guide the direction of investigation. To maximize the operating voltage output, some nonaqueous electrolytes such as ionic liquids and organic electrolytes that provide a two or three times wider working voltage window than the aqueous ones have been studied as desirable candidates. It is of high importance to explore nonaqueous electrolytes to obtain higher energy/power density, which will greatly pave the way for the practical production of electrochemical supercapacitors. In order to fully exploit the potential of transition metal oxide-based electrode materials for supercapacitors, it is imperative to optimize both synthesis parameters and material properties. The engineering factors of electrodes, including current collectors, electrolytes, membrane separators, counter electrodes, and packaging, still need a deeper investigation from fundamental investigation in the future.

Despite the challenges ahead, transition metal oxides utilizing as supercapacitive electrode material will be promising candidates for energy storage/conversation in the future. On one hand, systematical work should be performed on the current remarkable transition metal oxides to improve the electrochemical performance to the utmost. On the other hand, novel ideas such as discovering new metal oxide that is of excellent electrochemical performances are also urgently needed. In-depth understanding of the mechanisms of transition metal oxides for supercapacitors will

greatly promote the whole industrial development of the supercapacitors. All in all, with sustained and dedicated research efforts, these fascinating transition metal oxides nanomaterials will offer a new avenue to make the attractive electrochemical supercapacitors commercially viable.

References

1. Aricò AS, Bruce P, Scrosati B, Tarascon J-M, Van Schalkwijk W (2005) Nanostructured materials for advanced energy conversion and storage devices. *Nat Mater* 4(5):366–377
2. Simon P, Gogotsi Y (2008) Materials for electrochemical capacitors. *Nat Mater* 7(11):845–854
3. Conway B, Pell W (2003) Double-layer and pseudocapacitance types of electrochemical capacitors and their applications to the development of hybrid devices. *J Solid State Electrochem* 7(9):637–644
4. Lang X, Hirata A, Fujita T, Chen M (2011) Nanoporous metal/oxide hybrid electrodes for electrochemical supercapacitors. *Nat Nanotechnol* 6(4):232–236
5. Simon P, Gogotsi Y, Dunn B (2014) Where do batteries End and supercapacitors begin? *Sci Mag* 343:1210–1211
6. Becker HI (1957) Low voltage electrolytic capacitor. Google Patents
7. Kötz R, Carlen M (2000) Principles and applications of electrochemical capacitors. *Electrochim Acta* 45(15):2483–2498
8. Largeot C, Portet C, Chmiola J, Taberna P-L, Gogotsi Y, Simon P (2008) Relation between the ion size and pore size for an electric double-layer capacitor. *J Am Chem Soc* 130(9):2730–2731
9. Xia K, Gao Q, Jiang J, Hu J (2008) Hierarchical porous carbons with controlled micropores and mesopores for supercapacitor electrode materials. *Carbon* 46(13):1718–1726
10. Yu C, Masarapu C, Rong J, Wei B, Jiang H (2009) Stretchable supercapacitors based on buckled single-walled carbon-nanotube macrofilms. *Adv Mater* 21(47):4793–4797
11. Futaba DN, Hata K, Yamada T, Hiraoka T, Hayamizu Y, Kakudate Y, Tanaike O, Hatori H, Yumura M, Iijima S (2006) Shape-engineerable and highly densely packed single-walled carbon nanotubes and their application as super-capacitor electrodes. *Nat Mater* 5(12):987–994
12. Liu C, Yu Z, Neff D, Zhamu A, Jang BZ (2010) Graphene-based supercapacitor with an ultrahigh energy density. *Nano Lett* 10(12):4863–4868
13. Deng W, Ji X, Gómez-Mingot M, Lu F, Chen Q, Banks CE (2012) Graphene electrochemical supercapacitors: the influence of oxygen functional groups. *Chem Commun* 48(22):2770–2772
14. Song W, Ji X, Deng W, Chen Q, Shen C, Banks CE (2013) Graphene ultracapacitors: structural impacts. *Phys Chem Chem Phys* 15(13):4799–4803
15. Trasatti S, Buzzanca G (1971) Ruthenium dioxide: a new interesting electrode material. Solid state structure and electrochemical behaviour. *J Electroanal Chem Interfacial Electrochem* 29(2):A1–A5
16. Alonso A, Ruiz V, Blanco C, Santamaria R, Granda M, Menendez R, De Jager S (2006) Activated carbon produced from Sasol-Lurgi gasifier pitch and its application as electrodes in supercapacitors. *Carbon* 44(3):441–446
17. Frackowiak E, Beguin F (2001) Carbon materials for the electrochemical storage of energy in capacitors. *Carbon* 39(6):937–950
18. Huang J, Sumpter BG, Meunier V (2008) A universal model for nanoporous carbon supercapacitors applicable to diverse pore regimes, carbon materials, and electrolytes. *Chem Eur J* 14(22):6614–6626

19. Snook GA, Kao P, Best AS (2011) Conducting-polymer-based supercapacitor devices and electrodes. *J Power Sources* 196(1):1–12
20. Snook GA, Chen GZ (2008) The measurement of specific capacitances of conducting polymers using the quartz crystal microbalance. *J Electroanal Chem* 612(1):140–146
21. Yuan C, Wu HB, Xie Y, Lou XWD (2014) Mixed transition-metal oxides: design, synthesis, and energy-related applications. *Angew Chem Int Ed* 53(6):1488–1504
22. Conway BE (1991) Transition from “supercapacitor” to “battery” behavior in electrochemical energy storage. *J Electrochem Soc* 138(6):1539–1548
23. Zhang LL, Zhao X (2009) Carbon-based materials as supercapacitor electrodes. *Chem Soc Rev* 38(9):2520–2531
24. Wu Z, Zhu Y, Ji X (2014) NiCo₂O₄-based materials for electrochemical supercapacitors. *J Mater Chem A* 2(36):14759–14772
25. Deng W, Ji X, Chen Q, Banks CE (2011) Electrochemical capacitors utilising transition metal oxides: an update of recent developments. *Rsc Adv* 1(7):1171–1178
26. Zheng J, Cygan P, Jow T (1995) Hydrous ruthenium oxide as an electrode material for electrochemical capacitors. *J Electrochem Soc* 142(8):2699–2703
27. Zheng J, Jow T (1995) A new charge storage mechanism for electrochemical capacitors. *J Electrochem Soc* 142(1):L6–L8
28. Sugimoto W, Iwata H, Yokoshima K, Murakami Y, Takasu Y (2005) Proton and electron conductivity in hydrous ruthenium oxides evaluated by electrochemical impedance spectroscopy: the origin of large capacitance. *J Phys Chem B* 109(15):7330–7338
29. Zhou Z, Zhu Y, Wu Z, Lu F, Jing M, Ji X (2014) Amorphous RuO₂ coated on carbon spheres as excellent electrode materials for supercapacitors. *Rsc Adv* 4(14):6927–6932
30. Cui B, Lin H, Liu Y-Z, Li J-B, Sun P, Zhao X-C, Liu C-J (2009) Photophysical and photocatalytic properties of core-ring structured NiCo₂O₄ nanoplatelets. *J Phys Chem C* 113(32):14083–14087
31. Marco J, Gancedo J, Gracia M, Gautier J, Rios E, Berry F (2000) Characterization of the nickel cobaltite, NiCo₂O₄, prepared by several methods: an XRD, XANES, EXAFS, and XPS study. *J Solid State Chem* 153(1):74–81
32. Wang X, Liu WS, Lu X, Lee PS (2012) Dodecyl sulfate-induced fast faradic process in nickel cobalt oxide-reduced graphite oxide composite material and its application for asymmetric supercapacitor device. *J Mater Chem* 22(43):23114–23119
33. Li Y, Hasin P, Wu Y (2010) Ni_xCo_{3-x}O₄ nanowire arrays for electrocatalytic oxygen evolution. *Adv Mater* 22(17):1926–1929
34. Rasiyah P, Tseung A, Hibbert D (1982) A mechanistic study of oxygen evolution on NiCo₂O₄. I. Formation of higher oxides. *J Electrochem Soc* 129(8):1724–1727
35. Hu C-C, Chang K-H, Lin M-C, Wu Y-T (2006) Design and tailoring of the nanotubular arrayed architecture of hydrous RuO₂ for next generation supercapacitors. *Nano Lett* 6(12):2690–2695
36. Ozolins V, Zhou F, Asta M (2013) Ruthenia-based electrochemical supercapacitors: insights from first-principles calculations. *Acc Chem Res* 46(5):1084–1093
37. Wang G, Zhang L, Zhang J (2012) A review of electrode materials for electrochemical supercapacitors. *Chem Soc Rev* 41(2):797–828
38. Han JH, Lee SW, Kim SK, Han S, Hwang CS, Dussarrat C, Gatineau J (2010) Growth of RuO₂ thin films by pulsed-chemical vapor deposition using RuO₄ precursor and 5% H₂ reduction gas. *Chem Mater* 22(20):5700–5706
39. Vetrone J, Foster C, Bai G, Wang A, Patel J, Wu X (1998) Growth, microstructure, and resistivity of RuO₂ thin films grown by metal-organic chemical vapor deposition. *J Mater Res* 13(08):2281–2290
40. Zhu Y, Ji X, Pan C, Sun Q, Song W, Fang L, Chen Q, Banks CE (2013) A carbon quantum dot decorated RuO₂ network: outstanding supercapacitances under ultrafast charge and discharge. *Energy Environ Sci* 6(12):3665–3675

41. Zhang J, Ma J, Zhang LL, Guo P, Jiang J, Zhao X (2010) Template synthesis of tubular ruthenium oxides for supercapacitor applications. *J Phys Chem C* 114(32):13608–13613
42. Chen Y-M, Cai J-H, Huang Y-S, Lee K-Y, Tsai D-S, Tiong K-K (2011) A nanostructured electrode of IrOx foil on the carbon nanotubes for supercapacitors. *Nanotechnology* 22 (35):355708
43. Chen Y, Cai J, Huang Y, Lee K, Tsai D (2011) Preparation and characterization of iridium dioxide-carbon nanotube nanocomposites for supercapacitors. *Nanotechnology* 22 (11):115706
44. Du D, Hu Z, Liu Y, Deng Y, Liu J (2014) Preparation and characterization of flower-like microspheres of nano-NiO as electrode material for supercapacitor. *J Alloys Compd* 589:82–87
45. Yu W, Jiang X, Ding S, Li BQ (2014) Preparation and electrochemical characteristics of porous hollow spheres of NiO nanosheets as electrodes of supercapacitors. *J Power Sources* 256:440–448
46. Yang Z, Xu F, Zhang W, Mei Z, Pei B, Zhu X (2014) Controllable preparation of multishelled NiO hollow nanospheres via layer-by-layer self-assembly for supercapacitor application. *J Power Sources* 246:24–31
47. Huang M, Li F, Ji JY, Zhang YX, Zhao XL, Gao X (2014) Facile synthesis of single-crystalline NiO nanosheet arrays on Ni foam for high-performance supercapacitors. *CrystEngComm* 16(14):2878–2884
48. Zhang X, Shi W, Zhu J, Zhao W, Ma J, Mhaisalkar S, Maria TL, Yang Y, Zhang H, Hng HH (2010) Synthesis of porous NiO nanocrystals with controllable surface area and their application as supercapacitor electrodes. *Nano Res* 3(9):643–652
49. Yang Q, Sha J, Ma X, Yang D (2005) Synthesis of NiO nanowires by a sol-gel process. *Mater Lett* 59(14):1967–1970
50. Cheng J, Cao G-P, Yang Y-S (2006) Characterization of sol-gel-derived NiO xerogels as supercapacitors. *J Power Sources* 159(1):734–741
51. Xia X-H, Tu J-P, Wang X-I, Gu C-D, Zhao X-B (2011) Hierarchically porous NiO film grown by chemical bath deposition via a colloidal crystal template as an electrochemical pseudocapacitor material. *J Mater Chem* 21(3):671–679
52. Justin P, Meher SK, Rao GR (2010) Tuning of capacitance behavior of NiO using anionic, cationic, and nonionic surfactants by hydrothermal synthesis. *J Phys Chem C* 114 (11):5203–5210
53. Vijayakumar S, Nagamuthu S, Muralidharan G (2013) Supercapacitor studies on NiO nanoflakes synthesized through a microwave route. *ACS Appl Mater Interfaces* 5 (6):2188–2196
54. Fan Z, Chen J, Cui K, Sun F, Xu Y, Kuang Y (2007) Preparation and capacitive properties of cobalt-nickel oxides/carbon nanotube composites. *Electrochim Acta* 52(9):2959–2965
55. Zhao B, Song J, Liu P, Xu W, Fang T, Jiao Z, Zhang H, Jiang Y (2011) Monolayer graphene/NiO nanosheets with two-dimension structure for supercapacitors. *J Mater Chem* 21 (46):18792–18798
56. Subramanian V, Zhu H, Vajtai R, Ajayan P, Wei B (2005) Hydrothermal synthesis and pseudocapacitance properties of MnO₂ nanostructures. *J Phys Chem B* 109(43):20207–20214
57. Tao J, Liu N, Ma W, Ding L, Li L, Su J, Gao Y (2013) Solid-state high performance flexible supercapacitors based on polypyrrole-MnO₂-carbon fiber hybrid structure. *Sci Rep* 3
58. Li X, Wang G, Wang X, Li X, Ji J (2013) Flexible supercapacitor based on MnO₂ nanoparticles via electrospinning. *J Mater Chem A* 1(35):10103–10106
59. Pang SC, Anderson MA, Chapman TW (2000) Novel electrode materials for thin-film ultracapacitors: comparison of electrochemical properties of sol-gel-derived and electrodeposited manganese dioxide. *J Electrochem Soc* 147(2):444–450
60. Kang J, Hirata A, Kang L, Zhang X, Hou Y, Chen L, Li C, Fujita T, Akagi K, Chen M (2013) Enhanced supercapacitor performance of MnO₂ by atomic doping. *Angew Chem* 125 (6):1708–1711

61. Zhang X, Zhao D, Zhao Y, Tang P, Shen Y, Xu C, Li H, Xiao Y (2013) High performance asymmetric supercapacitor based on MnO_2 electrode in ionic liquid electrolyte. *J Mater Chem A* 1(11):3706–3712
62. Xiong S, Yuan C, Zhang X, Xi B, Qian Y (2009) Controllable synthesis of mesoporous Co_3O_4 nanostructures with tunable morphology for application in supercapacitors. *Chem-Eur J* 15(21):5320–5326
63. Xia X-H, Tu J-P, Mai Y-J, Wang X-I, Gu C-D, Zhao X-B (2011) Self-supported hydrothermal synthesized hollow Co_3O_4 nanowire arrays with high supercapacitor capacitance. *J Mater Chem* 21(25):9319–9325
64. Dong X-C, Xu H, Wang X-W, Huang Y-X, Chan-Park MB, Zhang H, Wang L-H, Huang W, Chen P (2012) 3D graphene–cobalt oxide electrode for high-performance supercapacitor and enzymeless glucose detection. *ACS Nano* 6(4):3206–3213
65. Xu K, Li W, Liu Q, Li B, Liu X, An L, Chen Z, Zou R, Hu J (2014) Hierarchical mesoporous $\text{NiCo}_2\text{O}_4@ \text{MnO}_2$ core–shell nanowire arrays on nickel foam for aqueous asymmetric supercapacitors. *J Mater Chem A* 2(13):4795–4802
66. Chen H, Jiang J, Zhang L, Qi T, Xia D, Wan H (2014) Facilely synthesized porous NiCo_2O_4 flowerlike nanostructure for high-rate supercapacitors. *J Power Sources* 248:28–36
67. Dalvi AD, Bacon WG, Osborne RC (2004) The past and the future of nickel laterites. In: PDAC 2004 international convention, trade show & investors exchange. The Prospectors and Developers Association of Canada, Toronto, pp 1–27
68. Hench LL, West JK (1990) The sol–gel process. *Chem Rev* 90(1):33–72
69. Niederberger M (2007) Nonaqueous sol–gel routes to metal oxide nanoparticles. *Acc Chem Res* 40(9):793–800
70. Livage J, Henry M, Sanchez C (1988) Sol–gel chemistry of transition metal oxides. *Prog Solid State Chem* 18(4):259–341
71. Wei TY, Chen CH, Chien HC, Lu SY, Hu CC (2010) A cost-effective supercapacitor material of ultrahigh specific capacitances: spinel nickel cobaltite aerogels from an epoxide-driven sol–gel process. *Adv Mater* 22(3):347–351
72. Liu M-C, Kong L-B, Lu C, Li X-M, Luo Y-C, Kang L (2012) A sol–gel process for fabrication of $\text{NiO/NiCo}_2\text{O}_4/\text{Co}_3\text{O}_4$ composite with improved electrochemical behavior for electrochemical capacitors. *ACS Appl Mater Interfaces* 4(9):4631–4636
73. Kong L-B, Lu C, Liu M-C, Luo Y-C, Kang L (2013) Effect of surfactant on the morphology and capacitive performance of porous NiCo_2O_4 . *J Solid State Electrochem* 17(5):1463–1471
74. Wu YQ, Chen XY, Ji PT, Zhou QQ (2011) Sol–gel approach for controllable synthesis and electrochemical properties of NiCo_2O_4 crystals as electrode materials for application in supercapacitors. *Electrochim Acta* 56(22):7517–7522
75. Zhu Y, Ji X, Wu Z, Song W, Hou H, Wu Z, He X, Chen Q, Banks CE (2014) Spinel NiCo_2O_4 for use as a high-performance supercapacitor electrode material: Understanding of its electrochemical properties. *J Power Sources* 267:888–900
76. Feng S, Xu R (2001) New materials in hydrothermal synthesis. *Acc Chem Res* 34(3):239–247
77. Chen Y, Qu B, Hu L, Xu Z, Li Q, Wang T (2013) High-performance supercapacitor and lithium-ion battery based on 3D hierarchical NH_4F -induced nickel cobaltate nanosheet–nanowire cluster arrays as self-supported electrodes. *Nanoscale* 5(20):9812–9820
78. An C, Wang Y, Huang Y, Xu Y, Xu C, Jiao L, Yuan H (2014) Novel three-dimensional NiCo_2O_4 architectures: solvothermal synthesis and electrochemical properties. *CrystEngComm* 16(3):385–392
79. Zou R, Xu K, Wang T, He G, Liu Q, Liu X, Zhang Z, Hu J (2013) Chain-like NiCo_2O_4 nanowires with different exposed reactive planes for high-performance supercapacitors. *J Mater Chem A* 1(30):8560–8566
80. Liu X, Zhang Y, Xia X, Shi S, Lu Y, Wang XL, Gu C, Tu J (2013) Self-assembled porous NiCo_2O_4 hetero-structure array for electrochemical capacitor. *J Power Sources* 239:157–163

81. Wang X, Han X, Lim M, Singh N, Gan CL, Jan M, Lee PS (2012) Nickel cobalt oxide-single wall carbon nanotube composite material for superior cycling stability and high-performance supercapacitor application. *J Phys Chem C* 116(23):12448–12454
82. Shen L, Che Q, Li H, Zhang X (2014) Mesoporous NiCo₂O₄ nanowire arrays grown on carbon textiles as binder-free flexible electrodes for energy storage. *Adv Funct Mater* 24(18):2630–2637
83. Zhang G, Lou XWD (2013) Controlled growth of NiCo₂O₄ nanorods and ultrathin nanosheets on carbon nanofibers for high-performance supercapacitors. *Sci Rep* 3:1470
84. Zhu Y, Wu Z, Jing M, Song W, Hou H, Yang X, Chen Q, Ji X (2014) 3D network-like mesoporous NiCo₂O₄ nanostructures as advanced electrode material for supercapacitors. *Electrochim Acta* 149:144–151
85. Musiani M (2000) Electrodeposition of composites: an expanding subject in electrochemical materials science. *Electrochim Acta* 45(20):3397–3402
86. Du J, Zhou G, Zhang H, Cheng C, Ma J, Wei W, Chen L, Wang T (2013) Ultrathin porous NiCo₂O₄ nanosheet arrays on flexible carbon fabric for high-performance supercapacitors. *ACS Appl Mater Interfaces* 5(15):7405–7409
87. Yuan C, Li J, Hou L, Zhang X, Shen L, Lou XWD (2012) Ultrathin mesoporous NiCo₂O₄ nanosheets supported on Ni foam as advanced electrodes for supercapacitors. *Adv Funct Mater* 22(21):4592–4597
88. Huang L, Chen D, Ding Y, Wang ZL, Zeng Z, Liu M (2013) Hybrid composite Ni(OH)₂@NiCo₂O₄ grown on carbon fiber paper for high-performance supercapacitors. *ACS Appl Mater Interfaces* 5(21):11159–11162
89. Zhang G, Wang T, Yu X, Zhang H, Duan H, Lu B (2013) Nanoforest of hierarchical Co₃O₄@NiCo₂O₄ nanowire arrays for high-performance supercapacitors. *Nano Energy* 2(5):586–594
90. Chang S-K, Lee K-T, Zainal Z, Tan K-B, Yusof NA, Yusoff WMDW, Lee J-F, Wu N-L (2012) Structural and electrochemical properties of manganese substituted nickel cobaltite for supercapacitor application. *Electrochim Acta* 67:67–72
91. Shakir I, Sarfraz M, Rana UA, Nadeem M, Al-Shaikh MA (2013) Synthesis of hierarchical porous spinel nickel cobaltite nanoflakes for high performance electrochemical energy storage supercapacitors. *Rsc Adv* 3(44):21386–21389
92. Wu Z, Pu X, Zhu Y, Jing M, Chen Q, Jia X, Ji X (2015) Uniform porous spinel NiCo₂O₄ with enhanced electrochemical performances. *J Alloys Compd* 632:208–217
93. Tseng C-C, Lee J-L, Liu Y-M, Ger M-D, Shu Y-Y (2013) Microwave-assisted hydrothermal synthesis of spinel nickel cobaltite and application for supercapacitors. *J Taiwan Inst Chem Eng* 44(3):415–419
94. Hu C-C, Hsu C-T, Chang K-H, Hsu H-Y (2013) Microwave-assisted hydrothermal annealing of binary Ni–Co oxy-hydroxides for asymmetric supercapacitors. *J Power Sources* 238:180–189
95. Yuan C, Li J, Hou L, Lin J, Pang G, Zhang L, Lian L, Zhang X (2013) Template-engaged synthesis of uniform mesoporous hollow NiCo₂O₄ sub-microspheres towards high-performance electrochemical capacitors. *Rsc Adv* 3(40):18573–18578
96. Ding R, Qi L, Jia M, Wang H (2013) Hydrothermal and soft-templating synthesis of mesoporous NiCo₂O₄ nanomaterials for high-performance electrochemical capacitors. *J Appl Electrochem* 43(9):903–910
97. Padmanathan N, Selladurai S (2013) Sonochemically precipitated spinel Co₃O₄ and NiCo₂O₄ nanostructures as an electrode materials for supercapacitor. In: American Institute of Physics conference series, pp 1216–1217
98. Salunkhe RR, Jang K, Yu H, Yu S, Ganesh T, Han S-H, Ahn H (2011) Chemical synthesis and electrochemical analysis of nickel cobaltite nanostructures for supercapacitor applications. *J Alloys Compd* 509(23):6677–6682
99. Zhu Y, Wu Z, Jing M, Hou H, Yang Y, Zhang Y, Yang X, Song W, Jia X, Ji X (2015) Porous NiCo₂O₄ spheres tuned through carbon quantum dots utilised as advanced materials for an asymmetric supercapacitor. *J Mater Chem A* 3(2):866–877

100. Zhu Y, Pu X, Song W, Wu Z, Zhou Z, He X, Lu F, Jing M, Tang B, Ji X (2014) High capacity NiCo_2O_4 nanorods as electrode materials for supercapacitor. *J Alloys Compd* 617:988–993
101. Li L, Peng S, Cheah Y, Teh P, Wang J, Wee G, Ko Y, Wong C, Srinivasan M (2013) Electrospun porous NiCo_2O_4 nanotubes as advanced electrodes for electrochemical capacitors. *Chem Eur J* 19(19):5892–5898
102. Hsieh Y-C, Lee K-T, Lin Y-P, Wu N-L, Donne SW (2008) Investigation on capacity fading of aqueous $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ electrochemical capacitor. *J Power Sources* 177(2):660–664
103. Kong L-B, Lu C, Liu M-C, Luo Y-C, Kang L, Li X, Walsh FC (2014) The specific capacitance of sol-gel synthesised spinel MnCo_2O_4 in an alkaline electrolyte. *Electrochim Acta* 115:22–27
104. Chuang P-Y, Hu C-C (2005) The electrochemical characteristics of binary manganese-cobalt oxides prepared by anodic deposition. *Mater Chem Phys* 92(1):138–145
105. Li L, He F, Gai S, Zhang S, Gao P, Zhang M, Chen Y, Yang P (2014) Hollow structured and flower-like $\text{C@MnCo}_2\text{O}_4$ composite for high electrochemical performance in a supercapacitor. *CrystEngComm* 16(42):9873–9881
106. Xu Y, Wang X, An C, Wang Y, Jiao L, Yuan H (2014) Facile synthesis route of porous MnCo_2O_4 and CoMn_2O_4 nanowires and their excellent electrochemical properties in supercapacitors. *J Mater Chem A* 2(39):16480–16488
107. Wang Z, Zhang X, Li Y, Liu Z, Hao Z (2013) Synthesis of graphene- NiFe_2O_4 nanocomposites and their electrochemical capacitive behavior. *J Mater Chem A* 1(21):6393–6399
108. Senthilkumar B, Vijaya Sankar K, Sanjeeviraja C, Kalai Selvan R (2013) Synthesis and physico-chemical property evaluation of PANI- NiFe_2O_4 nanocomposite as electrodes for supercapacitors. *J Alloys Compd* 553:350–357
109. Sen P, De A (2010) Electrochemical performances of poly (3, 4-ethylenedioxythiophene)- NiFe_2O_4 nanocomposite as electrode for supercapacitor. *Electrochim Acta* 55(16):4677–4684
110. Xiao K, Xia L, Liu G, Wang S, Ding L-X, Wang H (2015) Honeycomb-like NiMoO_4 ultrathin nanosheet arrays for high-performance electrochemical energy storage. *J Mater Chem A* 3(11):6128–6135
111. Peng S, Li L, Wu HB, Madhavi S, Lou XWD (2014) Controlled growth of NiMoO_4 nanosheet and nanorod arrays on various conductive substrates as advanced electrodes for asymmetric supercapacitors. *Adv Energy Mater* 5(2):1401172
112. Cai D, Liu B, Wang D, Liu Y, Wang L, Li H, Wang Y, Wang C, Li Q, Wang T (2014) Enhanced performance of supercapacitors with ultrathin mesoporous NiMoO_4 nanosheets. *Electrochim Acta* 125:294–301
113. Cai D, Liu B, Wang D, Liu Y, Wang L, Li H, Wang Y, Wang C, Li Q, Wang T (2014) Facile hydrothermal synthesis of hierarchical ultrathin mesoporous NiMoO_4 nanosheets for high performance supercapacitors. *Electrochim Acta* 115:358–363
114. Cai D, Wang D, Liu B, Wang Y, Liu Y, Wang L, Li H, Huang H, Li Q, Wang T (2013) Comparison of the electrochemical performance of NiMoO_4 nanorods and hierarchical nanospheres for supercapacitor applications. *ACS Appl Mater Interfaces* 5(24):12905–12910
115. Guo D, Zhang P, Zhang H, Yu X, Zhu J, Li Q, Wang T (2013) NiMoO_4 nanowires supported on Ni foam as novel advanced electrodes for supercapacitors. *J Mater Chem A* 1(32):9024–9027
116. Guo D, Luo Y, Yu X, Li Q, Wang T (2014) High performance NiMoO_4 nanowires supported on carbon cloth as advanced electrodes for symmetric supercapacitors. *Nano Energy* 8:174–182
117. Liu X, Zhang K, Yang B, Song W, Liu Q, Jia F, Qin S, Chen W, Lib J, Zhang Z (2015) Three-dimensional graphene supported nickel molybdate nanowires as novel ultralight and flexible electrode for supercapacitors. *arXiv preprint arXiv:150201059*

118. Yin Z, Zhang S, Chen Y, Gao P, Zhu C, Yang P, Qi L (2015) Hierarchical nanosheet-based NiMoO₄ nanotubes: synthesis and high supercapacitor performance. *J Mater Chem A* 3 (2):739–745
119. Cai D, Wang D, Liu B, Wang L, Liu Y, Li H, Wang Y, Li Q, Wang T (2014) Three-dimensional Co₃O₄@ NiMoO₄ core/shell nanowire arrays on Ni foam for electrochemical energy storage. *ACS Appl Mater Interfaces* 6(7):5050–5055
120. Ma X-J, Kong L-B, Zhang W-B, Liu M-C, Luo Y-C, Kang L (2014) Design and synthesis of 3D Co₃O₄@ MMoO₄ (M = Ni, Co) nanocomposites as high-performance supercapacitor electrodes. *Electrochim Acta* 130:660–669
121. Hong W, Wang J, Gong P, Sun J, Niu L, Yang Z, Wang Z, Yang S (2014) Rational construction of three dimensional hybrid Co₃O₄@ NiMoO₄ nanosheets array for energy storage application. *J Power Sources* 270:516–525
122. Guo D, Ren W, Chen Z, Mao M, Li Q, Wang T (2015) NiMoO₄ nanowire@ MnO₂ nanoflake core/shell hybrid structure aligned on carbon cloth for high-performance supercapacitors. *Rsc Adv* 5(14):10681–10687
123. Zhang Q, Deng Y, Hu Z, Liu Y, Yao M, Liu P (2014) Seurchin-like hierarchical NiCo₂O₄@ NiMoO₄ core-shell nanomaterials for high performance supercapacitors. *Phys Chem Chem Phys* 16(42):23451–23460
124. Ren W, Guo D, Zhuo M, Guan B, Zhang D, Li Q (2015) NiMoO₄@ Co(OH)₂ core/shell structure nanowire arrays supported on Ni foam for high-performance supercapacitors. *Rsc Adv* 5(28):21881–21887
125. Liu M-C, Kong L-B, Lu C, Ma X-J, Li X-M, Luo Y-C, Kang L (2013) Design and synthesis of CoMoO₄-NiMoO₄·x H₂O bundles with improved electrochemical properties for supercapacitors. *J Mater Chem A* 1(4):1380–1387
126. Senthilkumar B, Meyrick D, Lee Y-S, Selvan RK (2013) Synthesis and improved electrochemical performances of nano β-NiMoO₄-CoMoO₄·xH₂O composites for asymmetric supercapacitors. *Rsc Adv* 3(37):16542–16548