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Frontiers in nano-architectured carbon–metal oxide electrodes for supercapacitance energy storage: a review

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Abstract

Supercapacitor (SC) is an energy storage technology that bridges the gap between conventional capacitors and rechargeable batteries. Emerging nano-architectured carbon–metal oxide composites are promising for electrode designs for supercapacitors due to their unique strategy utilizing electrochemical double-layer capacitance (EDLC) and pseudo-capacitance together in single cell to optimize the energy storage ability and electrochemical stability. In recent years, technologies of integrating different metal oxide into single-walled/multi-walled carbon nanotubes (CNTs), graphene/reduced graphene oxide (rGO) and carbon nanofiber (CNF) and/or carbon fiber paper (CFP) have been reported with the focus of the nano-architecture electrodes. This paper provides a review of the frontiers with respect to incorporation of metal oxides into the carbon nanomaterials for capacitive energy storage improvements. Several key performance parameters in terms of specific capacitance, energy density, power density and cyclic stability along with the challenges and design trends are discussed and summarized.

Introduction

Since the fossil fuel depletion has been identified as a future challenge, the needs of efficient, renewable, sustainable energy sources are very urgent in the long term [1-3]. Energy storage systems, such as fuel cells, batteries and supercapacitors, are good power sources for electronic devices ranging from cellphones to vehicles. Among these energy storage technologies, fuel cells have the highest energy density, but their power densities are the lowest and unit size/weight usually is large. Batteries have good energy density, but their power densities are low and cycle lives are limited. Supercapacitors, also called electrochemical double layer capacitors (EDLC), are promising energy storage devices which provide higher energy density than conventional capacitors and higher power density than batteries, hence they have drawn a lot of attention due to their unique characteristics, such as high power density, fast charging/discharging rate and large cycling stability [4-6].

It is highly demanded to improve energy density and power density for supercapacitors. According to energy storage mechanism, the capacitance (C_{dl}) and energy stored (E) of EDLC can be expressed by the equation: [7]

$$C_{dl} = \frac{\varepsilon_r \varepsilon_0 A}{d} \quad (1)$$

$$E = \frac{1}{2} C_{dl} V^2 = \frac{1}{2} \varepsilon_r \varepsilon_0 V_b^{\,2} \quad (2)$$

where ε_r is the relative dielectric constant in the double layer, ε_0 is the permittivity of free space, A is the surface area of the electrode, and d is the thickness of the double layer. Commercially available SCs maximize the geometric term (A/d), while the electrolytes used have low ε_r, and small break down voltages (V_b). Advanced SC concepts would focus on maximizing both geometric and materials parameters to provide energy densities greater than current Li-ion batteries, limit maintenance, and long operational life spans (e.g. 10 years) with great recharge cycles (e.g. 100,000). There is an unmet need to develop a breakthrough solution that would complement existing EDLC structures with significantly enhanced energy storage capacity.

For capacitive energy storage of high density and power that compels to rechargeable batteries, it is required that the electrode materials will withstand high electric fields and maintain a high dielectric constant. Some efforts have been taken on dielectric composites with focusing on the enhancement of the dielectric permittivity using ferroelectric metal oxides $Pb(Zr,Ti)O_3$ (PZT), $Pb(Mg0.33Nb0.77)O_3$-$PbTiO_3$ (PMNT), and $BaTiO_3$ (BT) [8]. Some of the electroactive metal oxide, e.g. ruthenium oxide (RuO_2), manganese oxide (MnO_x), nickel oxide (NiO), etc. offer fast and reversible redox reactions, used as supercapacitor electrodes (also called pseudocapacitors), [7,9] resulting in higher energy density capacity but some sacrifices of power density and cycle life. In order to overcome this limit and improve the performance, progresses have been made in recent years on incorporating a variety of metal oxides in carbon nanomaterials for the development of next generation supercapacitors.

Carbon nanomaterials (CNM), such as carbon nanotubes (CNTs), graphene and reduced graphene oxide (rGO), graphene nanofoam (GF) and carbon nanofibers (CNFs) possess unique size and surface dependent (e.g., morphological) properties and excellent intrinsic physical (e.g., electrical, thermal, chemical and mechanical) properties which are ideal for application in supercapacitors. The first generation CNM-based supercapacitor took advantage of the

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exceptionally high surface areas, relatively high electronic conductivity to assemble an electrode for EDLC capacitor [10,11]. Moreover, the first generation CNM-based supercapacitors have shown improved capacitance and recycling rate capability over the traditional industrial electrode materials such as activated carbon electrodes. In order to further improve the energy density and overall performance of CNM supercapacitors, a new type of the next generation supercapacitors is emerging by utilizing unique strategies to control the nano-architecture of the dielectric metal-oxide (MO) at the surface of porous, conductive CNM scaffold. The CNM scaffold is used as supportive electrodes to realize ultra-high specific surface area (SSA) and to stabilize an additional active MO layer, e.g. by integrating super- or pseudo-capacitance with EDLC.

In this mini-review, recent research progresses (2013-2015) in supercapacitors with the focus of nano-architectured carbon-metal oxide electrodes are reviewed based on a number of representative research publications in the past three years. Different CNM utilized for metal oxide supercapacitors are classified according to different carbon structure types, and the electrochemical energy storage performances are presented with a summary table of recently reported results. In the last, the outlook and challenges of these strategies are briefly discussed.

Carbon nanomaterials-metal oxide for the next generation supercapacitors

As abovementioned, carbon nanomaterials (CNM), e.g. CNTs, rGOs, intrinsically own high electrical conductivity, high charge transfer capability, large SSA mesoporosity, and high electrolyte accessibility, which make them attractive using as electrode materials. Since CNT [12] and graphene [13] were introduced to the applications of supercapacitor, tremendous progress has been made in the period of 1999-2012 including, but not limited to, zero-dimensional carbon onions, [14] one-dimensional highly densely packed single-walled carbon nanotubes (SWNT) [15] and two-dimensional activated graphene based supercapacitor [16]. In 2006, J. Chmiola *et al.* [17] found that SSA, pore size distribution (PSD) and pore shape are key factors of a high performance EDLC supercapacitor. Lots of efforts have been made after that, e.g. KOH thermal activation, [18-21] microwave activation, [16] to increase SSA and control PSD. These pioneer efforts have shown the advances in increasing surface area and energy storage performance. However, the activation treatment may undermine the stability of CNM, and the effective surface area is limited by the theoretical value [22]. Most of the reported EDLC capacitors have a specific capacitance around 50-300 F/g [23,24]. In contrast, carbon nanomaterials-metal oxide-based supercapacitors (CNMO-SC), notably the next generation supercapacitors, are promising candidates which may produce ultrahigh energy storage capacity (> 1000 F/g) and battery comparable energy density, while at relatively low cost [25,26]. Thus, a number of recent CNMO-SC studies categorized by the type of carbon nanomaterials are reviewed and discussed below.

Carbon nanotubes-metal oxide based supercapacitors

CNT is well-known for its outstanding electrical and mechanical properties such as high length to diameter ratio (up to 132,000,000:1) and intrinsically metallic property [27]. Its exceptional vertical growth mechanism facilitates the formation of a continuous network for perfect charge transport along the longitude direction. This mechanism can also form an excellent three-dimensional template known as "CNT-forest" for depositing metal-oxide to improve the energy storage capability. Carbon nanotube-forest (CNT-F) template has been coupled with MnO_2, [28] NiO, [29] Co_3O_4 [30] to form the CNMO-SCs. The CNT-F-MnO_2 nanocomposite was designed and prepared by electrodepositing MnO_2 onto plasma enhanced chemical vapor deposition (PECVD) grown CNT-F. A comparison between the cyclic voltammograms (CV) of potentiostatic–deposited MnO_2 on CNT-F, galvanostatic–deposited MnO_2 on CNT-F and bare CNT-F was performed and reported [28]. The CV of potentiostatic-deposited MnO_2 on CNF has a better rectangular shape comparing to potentiostatic MnO_2 without clear redox peaks at different scan rates (10 mV/s-150 mV/s). A huge increase of CV of galvanostatic–deposited MnO_2 on CNT-F comparing to pure CNT-F was observed which is similar to CNT-F-NiO composite. In another study, CNT-F was firstly grown on a silicon substrate using a film of Fe/Al/Mo as both catalyst materials and current collecting layer, followed with an electrodeposition which insert nickel nanoparticles into the 3D structure to improve the pseudocapacitance [29]. The CNT-F-NiO nanocomposite delivers a 5.7 times higher capacitance comparing to pure CNT-F grown by chemical vapor deposition (CVD). There's no apparent current amplitude degradation after 100 cycles and only 5.8% capacitance drop after 10000 cyclic voltammetry tests, which indicates a good stability of the electrode.

Similar CVD technique was used to grow CNT-F on silicon wafer for the CNF-Co_3O_4 hybrid 3D architecture [30]. ZnO and MnO_2 were also introduced to the CNT-F by using a microwave-assisted chemical technique as comparisons (Figure 1). The CNT-F/Co_3O_4 composite exhibited the best performance with an areal capacitance of 30.84 mF/cm^2, a specific capacitance of 123.94 F/g, and a coulombic efficiency of about 87-92% over 1000 charge/discharge cycles. It shows that elastocapillary condensation and bending were useful tools for nano-architecture alternation.

In addition to CNT-F, CNT individual tubes were also coated with MnO_2 [31-33] for supercapacitor electrodes. For an example, Good capacitance around 150-250 F/g and areal capacitance of 4.9 F/cm^3 were demonstrated of a CNT/MoO_3 electrode by wet chemical deposition and electrodeposition [33]. Another interesting study using nylon fiber based CNT-MnO_2 electrode assembly has been reported by Choi *et al.* [34] *via* electrochemical deposition. It presented a less than 15% decrease in capacitance when reversibly stretched by 150%, suggesting high flexibility as a stretchable, wearable electrode for supercapacitor applications.

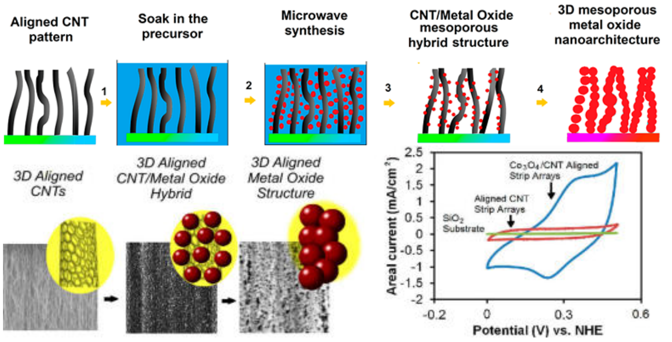

Figure 1. (Top panel) Schematic representation of the experimental steps showing the fabrication of 3D mesoporous hybrid CNT/oxide architectures and 3D mesoporous metal oxide structures; (b) (Lower panel) Scanning electron microscopy (SEM) images of 3D aligned CNTs, metal oxide hybrid electrodes, and representative cyclic voltammograms [30].

Graphene/reduced graphene oxide-metal oxide based supercapacitors

Graphene is two-dimensional (2D) carbon structure composed of honeycomb-shaped crystal lattice. It is the thinnest known material in the world and possesses a theoretical specific surface area of 2620 m^2/g as well as extreme electrical conductivity [35]. In the next generation supercapacitor application, graphene is usually utilized as the perfect current collector/support to substitute traditional conductive substrates such as Al, Cu, Indium tin oxide(ITO), etc. [36]. Several strategies have been reported using graphene coupled with MnO_2, [37-39] $Ni(OH)_2$, [40] $CoMoO_4$, [41] Mn_3O_4, [42] Co_3O_4, [43] and/or MoO_3 [44]. The graphene-MnO_2 nanocomposites have been demonstrated by different methods. In 2013, a facial assembly of δ-MnO_2 nanosheets and reduced graphene-oxide (rGO) flakes was demonstrated to fabricate a planar supercapacitor [37]. The synergic effects of the electrostatic effects and the morphology induced interactions strengthened the integration of rGO and MnO_2 nanosheets. In the same year, graphene aerogels (GA) were synthesized *via* sol–gel method as the template for electrodeposited MnO_2 [39] The as-prepared GA possess a high specific surface area of 793 m^2/g and a high pore volume of 3 cm^3/g. The specific capacitance is 410 F/g and only decays 5% after 50,000 cycles. The good capacity and stability may be attributed to the structural advantages and three-dimensionally network of the GA support. Graphene is used as not only a mesporous/microporous support, but also a mechanical support in a relative large unit scale (~2 cm^2) for supercapacitor applications [45]. Two novel CVD synthesis of graphene foam (GF) on nickel foam followed by hydrothermal deposition of MnO_2 [38] and $CoMoO_4$ [41] were reported to show the outstanding electrical and mechanical properties of 3D graphene foam [38,41]. The prepared graphene foam has a relatively low SSA due to the large pore size of several hundred micrometers. However the graphene acts as both the conductive and mechanical support all by itself, which means there's no need to exploit metal current collector. The overall performance of GF-Ni(OH) and GF-$CoMoO_4$ are 144 F/g and 439.7 F/g in specific capacitance and 44 kW/kg and 900 W/kg in power density [38,41] which indicate the structural and electrochemical superiority of GF for flexible, foldable and stretchable supercapacitors. Figure 2 shows a porous structure with an interconnected 3D scaffold of nickel which was served as a template for the growth of 3D graphene, and morphological structures. This work illustrates a method for the development of 3-D-graphene porous skeleton electrode incorporating $CoMoO_4$ as stable electrode for supercapacitors, with excellent pseudocapacitive performance.

A few researchers reported that graphene nano-composites with Mn_3O_4 and Co_3O_4 prepared using an in-solution process [42-44]. Specifically, GO was firstly synthesized with Hummers method, then precursor solutions were mixed with GO followed with a thermal and/or microwave-assist treatment to deposit Mn_3O_4/Co_3O_4 onto the rGO surface. Their specific capacitance reaches 344 F/g and 712 F/g, energy density are as high as 93 Wh/kg, 52.84 Wh/kg. Their high performance can attribute to the more densely packed structure compared to graphene foam, which provides a highly conductive network and excellent interfacial contact for electron transport during the charge/discharge processes. Furthermore, a notable approach [46] is reported using graphene-wrapped and microwave-assisted intercalating Co_3O_4 to form a hybrid supercapacitor electrode and demonstrate 712 F/g capacitance and decent energy density. The intercalation of cobalt oxide nanoparticle between graphene layers and external graphene-wrapping provides the excellent cycling stability.

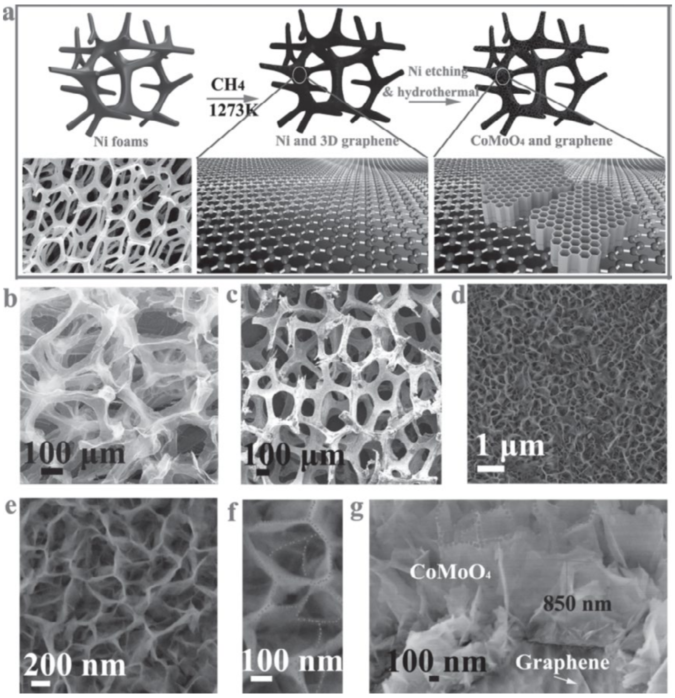

Figure 2. Growth mechanism and the morphology of honeycomb-like $CoMoO_4$ -3D graphene hybrid electrodes. (a) the typical synthesis procedure of the graphene hybrid electrodes, (b) SEM images of (b) 3D graphene, (c-f) honeycomb-like strongly coupled $CoMoO_4$ -3D graphene hybrid at various magnification. (g) Cross-section SEM image of NHC-like $CoMoO_4$-3D graphene hybrid [41].

Electrospun carbon nanofiber-metal oxide based supercapacitors

Electrospun carbon nanofibers (ECNF) is well known for its large porosity, high conductivity, cheap and freestanding nature as electrode materials for EDLC applications [47,48]. Moreover, ECNF structures can also be served as scaffolds to uniformly support nanostructured metal oxide because of their reliable 3D-network structure. Carbon nanofibers (CNF) and carbon fiber paper (CFP) are essentially the same material with length of tens of micrometers and diameter range from 30 nm to 220 nm. In recent years, much efforts have been focused on using ECNF synthesized by different methods as the backbone to support metal oxide pseudocapacitive materials, significantly enhancing the rate capability by shortening the distance of electron transport [49]. Activation treatment/dip-coating/electrochemical depositions are mostly used methods in ECNF-metal oxide composites for supercapacitor applications. Activated ECNF has been coupled with Co_3O_4, [50] SnO_2, [51] ZnO [52] and V_2O_5 [53] by incorporating different metal oxide precursors(e.g. $Co(acac)_2$, $SnCl_2 .2H_2O$, $Zn(O_2CCH_3)_2$, or V_2O_5 in DMF) into polyacrylonitrile (PAN) *via* one-step electrospinning method. The advantage of this method is the facial synthesis/processes and ultrahigh surface area (>1000 m^2/g) compared to non-activated ECNF (<100 m^2/g) [54]. The activation treatment increases the SSA but undermines the internal structure of the ECNF network, therefore the cyclic stability of these electrodes are lowered. Among these reports, the activated ECNF-Co_3O_4 electrode shows a relatively high specific capacitance of 556 F/g with an excellent cyclic performance [50]. Figure 3 illustrates (A) the co-electrospinning setup for the preparation process of the hollow Co_3O_4 NPs-CNFs *via* an electrospinning and post annealing strategy and (B) images of the

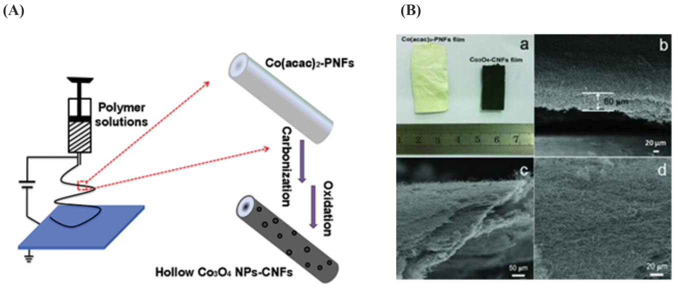

Figure 3. (A) Ideal schematic illustration for obtaining porous ECNF electrodes synthesized using co-electrospinning method with H_2-reduction and post annealing strategy; and (B) the photograph of Co(acac)$_2$-PNFs and Co_3O_4-ECNFs hybrid films. b,c) The side-view SEM images and d) the top-view SEM image of the Co_3O_4-ECNFs hybrid films. (cited from ref.50)

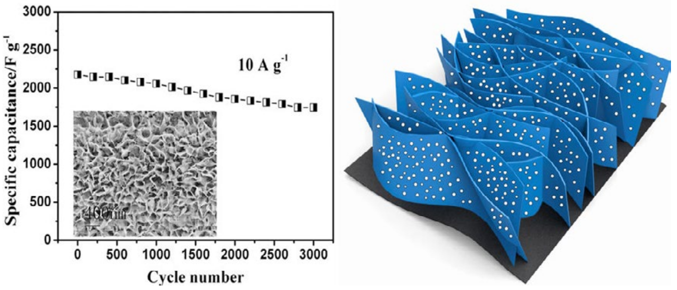

Figure 4. Ultrathin porous $NiCo_2O_4$ nanosheet arrays on flexible carbon fabric for high-performance supercapacitors, $NiCo_2O_4$ as pseudocapacitive material with higher specific capacitance is prepared as ultrathin nanosheet arrays adhered on flexible CFP as supercapacitor electrode of high performance and long cycling life [57].

Co_3O_4-ECNFs hybrid film electrodes.

Dip-coating provides a simple and low cost solution for depositing metal-oxide onto ECNF. Heat assisted MnO_2 dip-coating deposition has been applied onto ECNF surface for supercapacitor application with a wide voltage range of 0–2.0 V [55]. The good capacitance and cyclic performance afford a convenient and efficient way to construct electrodes based on freestanding materials for energy storage system. Electrodeposition is an unique and powerful method which can quantitatively control the morphorlogy of the metal oxide active materials and easily to scale up for large amount production. A novel modified Te-nanowire template directed hydrothermal synthesis of carbon nanofiber followed with electrodeposition of ultrathin $NiCo_2O_4$ is reported by Zhang *et al.* [56]. The ECNF-$NiCo_2O_4$ hierarchical hybrid nanostructures have great potential as advanced electrode materials for high-performance supercapacitors.

Carbon fiber paper-metal oxide based supercapacitors

Carbon fiber paper (CFP), also known as carbon fabric or carbon cloth, is a commercial product physically similar to ECNF. It has good electric conductivity, excellent mechanical property, cheap and easy to be scaled up, yet consists of microsized carbonfibers (diameter range from 5-15 um). $NiCo_2O_4$ is the most popular metal oxide material coupled with CFP in the forms of $NiCo_2O_4$ nanorod/nanosheet arrays, [57] CFP-$NiCo_2O_4$@NiO, [58] CFP-Ni/Co layered double hydroxide (LDH) [59] and CFP-Ni/Co LDH@ZnO [60]. $NiCo_2O_4$ precursor was electrodeposited onto CFP to form ultrathin (10 nm) nanosheet arrays. The interconnected structure with good conductivity of the composites delivered an astonishing high specific capacitance of 2658 F/g and long cycling life [57]. $NiCo_2O_4$@NiO core–shell hetero-nanowire on CFP has been assembled by stepwise dip-coating to fabricate the $NiCo_2O_4$@NiO-CFP for a high-performance flexible all-solid-state supercapacitor [58]. Ni/Co LDH was fabricated by electrodepositing Co_xNi_{1-x} hydroxide coatings onto CFP supported hydrothermal synthesized $NiCo_2O_S$ nanowire arrays [60]. A facile two-step hydrothermal synthesis has been applied to CFP to form a CFP-Ni/Co LDH@ZnO nanowires hybrid array for supercapacitor application [60] All three designs have shown extraordinary performance in captivity, stability and simplicity. Their high specific capacitances (1500-1900 F/g), energy density (33-45 Wh/kg) and power density (41-46 kw/kg) can be attributed to the unique 3D micrometer architecture of the CFP-Ni/Co@Metal oxide hybrid structures.

Other than $NiCo_2O_4$ based composites, $NiCo_2S_4$ [61] VO_x [62] and NiO [63] were also integrated onto CFP for high energy storage applications. $NiCo_2O_4$ single crystalline nanotube arrays have been grown on CFP serving as not only an excellent pseudocapacitive material but also a scaffold facilitating ion diffusion [61]. VO_x and NiO have also been deposited onto CFP with different methods e.g. hydrothermal, dip-coating and electrodeposition [62-63]. These all show a good potential for the development of light, compact, and high-performance supercapacitors.

Hybrid CNM-metal oxide based supercapacitors

Carbon nanotube, graphene and carbon fiber are the most

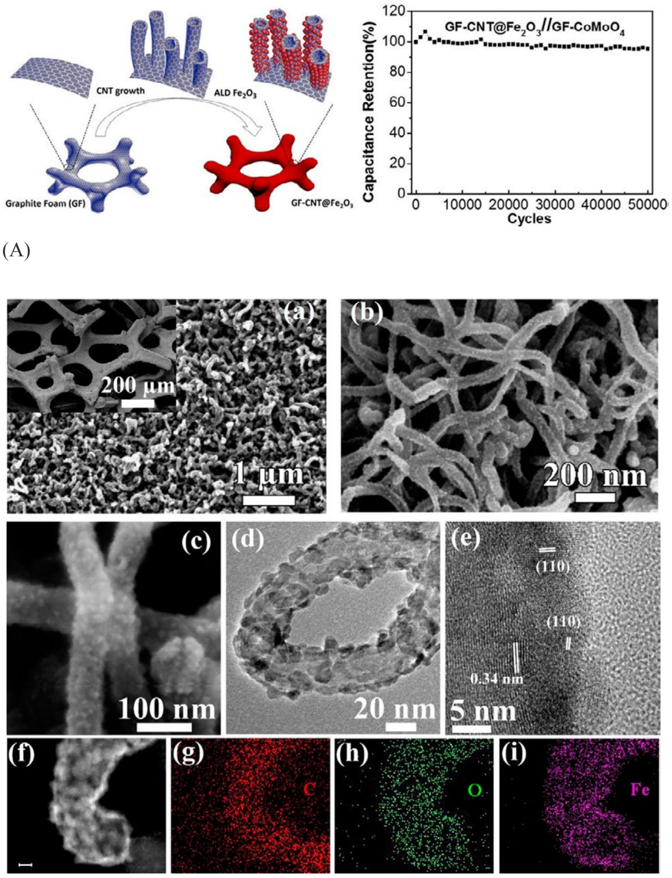

Figure 5. (A) Schematic illustration of formation of a Graphite foam@CNT-Fe_2O_3 and extraordinary energy storage performance; (B) SEM and TEM characterization of GF_CNT@Fe_2O_3. (a_c) SEM and (d_e) HRTEM images of GF_CNT@Fe_2O_3. (f)HAADF_STEM image of a single CNT@Fe_2O_3 and (g-i) the corresponding STEM element mapping. The scale bar in (f) is 10 nm [64].

Table 1. A summary of representative carbon nanomaterials-metal oxide supercapacitance energy storage studies in recently years (since 2013).

Electrode materials	**Metal oxide**		**Capacitance (F/g)$^{\#}$**	**Energy density (Wh/kg)$^{\#}$**	**Power density (kW/kg)$^{\#}$**	**Stability**		**Ref.**
	Materials	**Method**				**cycle**	**%**	
CNT-forest (CNT-F) or CNT based								
CNT-F	MnO_2	EC deposit	642	-	-	-	-	[28]
CNT-F	Ni/NiOx	EC deposit	1.3 F/cm^3	-	-	10000	94.2	[29]
CNT-F	Co_3O_4	microwave	124			1000	92.0	[30]
CNT	MnO_2	wet coating	154	-	-	-	-	[31]
CNT	MnO_2	EC deposit.	247	-	-	2000	94.7	[32]
CNT	MnO_2/MO_3	EC deposit	4.9F/cm^3	11.2	5.5	5000	83.0	[33]
CNT	MnO_2	EC deposit	41mF/cm^2	2.6 mWh/cm^2	67mW/cm^2	-	-	[34]
Graphene foam (GF), reduced graphene oxide (rGO) based								
GF	MnO_2	hydrothermal	240	8.3	20	1000	90	[38]
GF	$CoMoO_4$	hydrothermal	2741	37.25	0.9	10000	87.4	[41]
rGO	MnO_2	vacuum filtration	267	18.6	12.6	7000	92.0	[37]
rGO	MnO_2	EC deposit	410			50000	95.0	[39]
rGO	Mn_3O_4	Layer-by-layer deposition	344	93	10	3000	87.0	[42]
rGO	Co_3O_4	Precipitation calcination	636	30.2	3.75	1000	95.0	[43]
rGO	MoO_2	Annealing coating	404	55	0.4	5000	80.0	[44]
rGO	Co_3O_4	Microwave	712	51	1	10000	100	[46]
Electrospun carbnon nanofiber (ECNF), carbon nanofiber (CNF) or carbon fiber paper (CFP) based								
ECNF	Co_3O_5	mix-electro-spinning	556			2000	99.0	[50]
ECNF	SnO_2	Co-electro-spinning	289	7.7	8	3000	97.0	[51]
ECNF	ZnO	Co-electro-spinning	178.2	17.8	4.0	1000	75.0	[52]
ECNF	V_2O_5	Co-electro-spinning	74	68.5	20	-	-	[53]
CNF	MnO_2	Chemical growth	56.8	30.6	0.20	5000	94.0	[55]
CNF	$NiCo_2S_4$	Thermal-chemical growth	942			2400	96.4	[56]
CFP	$NiCo_2O_4$	EC deposit	2658			3000	80.0	[57]
CFP	$NiCo_2O_4$ @NiO	thermal co-deposit	1500	33	41.25	2000	81.3	[59]
CFP	Ni-Co hydroxide	hydrothermal	1927	45.6	46.1	3000	96.0	[60]
CFP	$NiCo_2S_4$	Thermal-chemical growth	2.41 F/cm			2000	96.0	[61]
CFP	VO_x	hydrothermal	298	0.61 mWh/cm^3	0.85 W/cm^3	10000	87.5	[62]
CFP	NiO	hydrothermal	0.93 F/cm	-	-	10000	70.0	[63]
Two carbon nanomaterials (CNM) hybrid-based								
GF + CNF	Fe_2O_3	ALD	2555	74.7	1.4	50000	95.4	[64]
GF+CNT	RuO_2	Sol-gel	503	39.3	128	8100	106	[65]
GF +CNF	MnO_2	Microwave	948	53.4	332.5	1000	94.1	[66]
rGO+CNT	MnO_x	EC deposit	1200	46.2	33.2	200	62.0	[67]
rGO+CNT	MnO_2	Thermal growth	126	28.33	5	2500	83.0	[68]
rGO+CNT	FeOOH	hydrolysis	267	30.4	0.24	1000	89.0	[69]
CNF+G	FeN	ALD	58	15.4	6.4	20000	99.0	[70]
CNF+rGO	$Ni(OH)_2$	EC-deposit	1235			500	80.0	[71]
CFP+rGO	MnO_2	chemical	393			2000	98.5	[72]

$^{\#}$ if not specified other unit;

promising carbon materials for energy storage applications. Each of them has some superior properties, e.g. physical, morphological. Therefore, the structures that bundle multiple CNM together as hybrid materials are very attractive since they may hold their intrinsic properties and granted new characteristics prior to single CNM. Graphene foam was utilized with CNT by coupling with various metal oxides for high performance supercapacitors. Graphene foam@CNT with Fe_2O_3 [64] RuO_2 [65] and MnO_2 [65] were developed as novel 3D hierarchical structure. Atomic layer deposition (ALD) and modified sol-gel method were used to deposit Fe_2O_3 and RuO_2 onto the graphene foam@CNT forest hybrid structures [64].

Guan *et al*. developed a novel iron oxide decorated graphite foam-CNT forest [64]. The highest specific capacitance reaches 2555.6 F/g. The combination of CVD and ALD maximizes the conductivity and porous structure of graphene-like foam-CNT [64]. Similarly, synthesis of graphene@CNT on nickel foam followed with modified sol-gel method and dip-coating to deposit RuO_2 and MnO_2 onto the hybrid structure was demonstrated [65,66]. These superior designs optimize all CNM's characterizations to provide a conductive 3D network, large surface area to deposit metal oxides and react with electrolyte, cheap synthesis and processing, scaffold/support free from traditional metal current collector. MnO_x [67], MnO_2 [68] FeOOH [69] coupled with graphene@CNT composites were synthesized by chemical deposition and MnO_x was electrodeposited [69]. They all show good potential as supercapacitor electrodes.

Moreover, using graphene nanosheets coupled with CNT/CNF as hybrid materials for supercapacitor electrodes. Fe_2N [70] $Ni(OH)_2$ [71] and MnO_2 [72] were deposited onto CNF supported graphene flakes *via* different deposition methods, including ALD, hydrolysis/condensation, elecrodeposition and thermal assisted chemical coating. The interconnected flexible structures exhibit good electrochemical performances with high specific capacitance and cycling performance.

A summary and outlook

This paper has reviewed recent research progress in the CNM–metal oxide composites for supercapacitor electrodes. As a summary, Table 1 reports collective results of representative research publications regarding CNM-MO supercapactors for energy storage in recent three years. Apparently, this work has no way to cover all related research published in literature. From these limited, representative results, we conclude that:

(1) Nanomaterials and nanotechnology have opened up new frontiers in materials sciences and engineering to meet the demands for high energy storage supercapacitors by offering unique enabling technology and methods;

(2) Carbon nanomaterials intrinsically have excellent conductivity, large surface area, extensive options of chemically modification, inexpensive crude materials/processes and optimal mechanical property which are promising for next generation supercapacitors.

(3) Since the metal oxide with 3D scaffold/support is the key to the high-performance next generation supercapacitors, CNT-F, graphene foam and ECNF/CNF/CFP are the highlighted CNM candidates among the all CNM substrates mentioned in previous sections. Yet their energy density regarding to whole cell is still low compared to lithium battery.

(4) Hybrid CNM-metal oxide based supercapacitors, *i.e.* combining two or more CNMs, have the best performance regarding the capacitance, energy/power density, suggesting the future direction of the supercapacitor electrode development. Moreover, the deposition to control the morphology of the metal oxide is one of the key factors for energy storage.

(5) The deposition methods for metal oxide and post-treatment of the CMO-MO are important for energy storage performance. The ALD Fe_2O_3 demonstrates to date the best energy density, outstanding capacitance and high stability, however cost is high. Electrochemical deposition is a facial, applicable method and low cost with a various performance from good to excellent.

However, there remain challenges guide us to overcome the barrier of insufficient electrochemical capacity of CNM–metal oxide composites, especially the energy density and long life cycle stability. Some aspects should be considered for future optimization or development of new solutions, which may significantly affect the overall performance of the supercapacitor electrodes. Those are: (1) further optimizing the geometries or dimensions in nanoscale, the interconnection of CNM, 3D networks can largely facilitate the charge transfer; (2) optimization of the metal oxide interfaces for better charge exchange and stability, and control of the morphology of CNM-metal oxide, thus high V_b; (3) requirement of standard testing methods which will make the research results under comparable conditions.

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