frontiers in Materials

MINI REVIEW
published: 02 August 2017
doi: 10.3389/fmats.2017.00021

Recent Advancements in the Cobalt Oxides, Manganese Oxides, and Their Composite As an Electrode Material for Supercapacitor: A Review

Santosh J. Uke[1,2]*, Vijay P. Akhare[2], Devidas R. Bambole[1], Anjali B. Bodade[2] and Gajanan N. Chaudhari[2]

[1] J. D. Patil Sangludkar College, Daryapur, India, [2] Nanoscience Research Laboratory, Shri Shivaji Science College, Amravati, India

Recently, our modern society demands the portable electronic devices such as mobile phones, laptops, smart watches, etc. Such devices demand light weight, flexible, and low-cost energy storage systems. Among different energy storage systems, supercapacitor has been considered as one of the most potential energy storage systems. This has several significant merits such as high power density, light weight, eco-friendly, etc. The electrode material is the important part of the supercapacitor. Recent studies have shown that there are many new advancement in electrode materials for supercapacitors. In this review, we focused on the recent advancements in the cobalt oxides, manganese oxides, and their composites as an electrode material for supercapacitor.

Keywords: hybrid supercapacitor, cobalt oxide, manganese oxide, specific capacitance, specific surface area

OPEN ACCESS

Edited by:
Sravendra Rana,
University of Petroleum and Energy Studies, India

Reviewed by:
Zhengjun Zhang,
Tsinghua University, China
Hongchang Pang,
Dalian University of Technology (DUT), China

Correspondence:
Santosh J. Uke
santosh_uke@rediffmail.com

Specialty section:
This article was submitted to Nanoenergy Technologies and Materials, a section of the journal Frontiers in Materials

Received: *10 February 2017*
Accepted: *30 June 2017*
Published: *02 August 2017*

Citation:
Uke SJ, Akhare VP, Bambole DR, Bodade AB and Chaudhari GN (2017) Recent Advancements in the Cobalt Oxides, Manganese Oxides, and Their Composite As an Electrode Material for Supercapacitor: A Review. Front. Mater. 4:21. doi: 10.3389/fmats.2017.00021

INTRODUCTION

Energy storage has an equal importance as energy production. To face the global challenges, recently, our modern society demands lightweight, flexible, inexpensive, and environmentally friendly energy storage systems (Meng et al., 2010; Chodankar et al., 2015). Battery and supercapacitor are the major energy storage devices. But, slow charge–discharge rate, short life cycles, and high weight of battery limit its applications in portable and wearable devises (Meng et al., 2010). At present, supercapacitors have been receiving a great attention, because of their important features such as high energy density, high power density, light weight, fast charging–discharging rate, secure operation, and long life span (Jayalakshmi and Balasubramanian, 2008; Chodankar et al., 2015). The supercapacitor is also called electrochemical capacitor. This is used in various applications such as hybrid vehicles, power backup, military services, and portable electronic devises like laptops, mobile phones, wrist watches, wearable devised, roll-up displays electronic papers, etc. (Lee et al., 2011; Wang et al., 2012).

CLASSIFICATION OF THE SUPERCAPACITOR

On the basis of charge storage mechanism and material used as the electrode, the supercapacitors are divided into two categories: electrochemical double layer supercapacitors (EDLCs) and pseudocapacitor (Jayalakshmi and Balasubramanian, 2008). In EDLCs, the specific capacitance arises from the non-Faradaic charge storage mechanism between electrode and electrolyte interface (Jayalakshmi and Balasubramanian, 2008; Wang et al., 2012). The materials that have been used as electrode for EDLCs are porous carbon (Kang et al., 2015), SWNT (Liu et al., 2006), MWNT (Huang et al., 2014a), reduce graphine oxide (Zhang and Zhao, 2012), aerogel (Faraji and Ani, 2015), etc. In pseudocapacitor, the specific capacitance arises from Faradaic reaction at the electrode interface. The materials that have been studied as electrode for pseudocapacitors are transition metal oxides and conducting polymers (Wang et al., 2012).

In particular, the specific capacitance of the supercapacitors depends on the surface area and the pore size distribution of the electrode material. Compared with the transition metal oxides and conducting polymers, carbon and its different types have high surface area (3.270 m²g⁻¹) (Kang et al., 2015). However, this high surface area of carbon is not completely accessible for the electrolyte (Faraji and Ani, 2015). To overcome this shortcoming, the composites of carbon with transition metal oxides or conducting polymer have received great attention. These composite are also called hybrid materials. The use of hybrid material as an electrode in supercapacitors result in the third category of supercapacitors called hybrid supercapacitors. In hybrid supercapacitors, the specific capacitance arises from Faradic as well as non-Faradic charge storage mechanism at the electrode and electrolyte interface (Zhang et al., 2013; Pardieu et al., 2015).

PARAMETERS FOR SUPERCAPACITOR

The specific capacitance (C_s) (Fg^{-1}), energy density E (Wh kg^{-1}), power density P (kW kg^{-1}), and retention capacity or coulomb efficiency (η) are the crucial characteristics of the supercapacitor device. The (C_s) (Fg^{-1}) at the single electrode of the device is calculated given by,

$$C_s = \frac{1}{mV(V_c - V_a)} \int_{v_a}^{v_c} I(v)dV \qquad (1)$$

where m is the mass (g cm^{-1}) deposited, $I(v)$ is the response current (mA) of the electrode material for unit area, V is the scan rate, $V_c - V_a$ is the operational potential window in (V), V_a anodic current, and V_c cathodic current. Energy density E (Wh kg^{-1}) and power density P (W kg^{-1}) of supercapacitor are calculated using following relations as,

$$E = \frac{0.5 \times C_s \times (V_{max}^2 - V_{min}^2)}{3.6} \qquad (2)$$

$$P = \frac{E}{t_D} \qquad (3)$$

where C_s is specific capacitance (Fg^{-1}), V_{max} and V_{min} are the maximum and minimum voltage achieved during charging and discharging process, respectively, in volt (V), and t_D is the discharging time (s) for a cycle of the supercapacitor. The retention of specific capacitance is calculated using the relation,

$$\eta = \frac{t_D}{t_C} \qquad (4)$$

where t_C and t_D are the charge and discharge time (s), respectively, for a cycle of the supercapacitor (Wang et al., 2010; Dubal et al., 2012).

RECENT ADVANCES IN COBALT OXIDE SUPERCAPACITOR

The transition metal oxides have a great scientific significance. These are the basis of a variety of functional materials (Shinde et al., 2015). Among the various supercapacitor electrode materials, transition metal oxides offer high electronegativity, rich redox reactions, low cost, environmental friendliness, and excellent electrochemical performance. Different transition-metal oxides, such as IrO_2, RuO_2, Co_3O_4, MnO_2, Fe_2O_3, SnO_2,

TABLE 1 | Co_3O_4-based supercapacitors.

Sr. no.	Material	Method of synthesis	High surface area	Electrolyte	High Sp. capacitance	Retention	Year	Reference
1	Co_2O_3 on NiO substrate	Electrodeposition method		1 M KOH	345 Fg^{-1} at 20 mV s^{-1}	>50% after 200	2014	Sarma et al. (2014)
2	Co_3O_4-decorated graphene	Microwave-assisted method	–	1 M KOH	600 Fg^{-1} at 0.7 A g^{-1}	94.5% after 5,000 cycles	2015	Kumar et al. (2015)
3	Pongam seed shell-derived activated carbon and cobalt oxide (Co_3O_4) nanocomposite	KOH activation method	164 m^2 g^{-1}	1 M KOH electrolyte	94 Fg^{-1} at 1 A g^{-1}	88% after 1,000 cycles	2015	Madhu et al. (2015)
4	Co_3O_4/$NiCo_3O_4$ double-shelled nanocages	The facile synthesis	–	2 M KOH	972 Fg^{-1} at a current density of 5 A g^{-1}	92.5% after 12,000 cycles	2015	Hu et al. (2015)
5	Synthesized titania nanotube cobalt (CoS) sulfide composite	Electrodeposition method	–	1 M Na_2SO_3	400 Fg^{-1} at charge density 5 mA cm^{-2}	>80% after 1,000 cycles	2015	Ray et al. (2015)
6	Co_3O_4 nanotubes	Chemical deposition method		6 ML^{-1} KOH	574 Fg^{-1} at 0.1 A g^{-1}	95% after 1,000 cycles	2010	Xu et al. (2010)
7	Ultrafine Co_3O_4 nanocrystal electrode	Laser ablation in liquid method	–		177 Fg^{-1} at scan rate 1 mV s^{-1}	100% after 20,000 cycles	2016	Liu et al. (2016)
8	Cobalt tungstate ($CoWO_4$)	Chemical precipitation reaction	–	0.2 M H_2SO_4	378 Fg^{-1} at scan rate 2 mV s^{-1}	95.5% after 4,000 cycles	2016	Adib et al. (2016)

NiO, etc., have been extensively studied as the electrode material for supercapacitor (Luo et al., 2014). Among these, RuO_2 has been identified as a dominant candidate because it has high theoretical specific capacitance (1,358 Fg^{-1}), high electrical conductivity (300 S cm^{-1}), and high electrochemical stability (Yu et al., 2013). However, the high cost and toxicity associated with the RuO_2 limits its commercial applications (Deng et al., 2014).

Furthermore, the cobalt oxides have received significant interest in recent years because of their low cost, non-toxic, easy synthesis, and environmental friendly nature. The cobalt oxides have high theoretical capacitance (CoO: 4.292 Fg^{-1}, Co_2O_4: 3.560 Fg^{-1}) (Cheng et al., 2010; He et al., 2012). Additionally, cobalt oxides show excellent electrochemical behavior in alkaline as well as organic electrolyte. These have the ability to interact with the ions of the electrolyte at the surface as well as through the bulk of the material (Vijayakumar et al., 2013). The features of cobalt oxides such as morphology, structures, and dimension can be easily controlled *via* adjusting the preparative parameters such as, reaction temperature, reaction time, concentration of matrix solution, complexing agent, etc. (Wei et al., 2015a).

An optimize microstructure and controlled morphology of the material will enhance the specific surface area and pore size distribution, which facilitate the electrolyte ion transport in the material (Meher and Rao, 2011). Recently, many new approaches have been successfully in use to synthesize the meso and microporous nanostructure cobalt oxide materials such as hydrothermal method (Meher and Rao, 2011), chemical bath deposition method (Xu et al., 2010), hydrothermal precipitation method (Yu et al., 2009), solvothermal synthesis method (Yang et al., 2013), combustion synthesis method (Deng et al., 2014), microwave-assisted synthesis method (Vijayakumar et al., 2013), etc.

The specific capacitance of the cobalt oxide strongly depends on morphology, surface area, and pore size distribution. Recently,

TABLE 2 | MnO_2-based supercapacitor.

Sr. no.	Material	Method of synthesis	High surface area	Electrolyte	High Sp. capacitance	Retention	Year	Reference
1	Manganese oxide (MnO_2)/three-dimensional (3D) reduced graphene oxide (RGO)	Reverse microemulsion (water/oil) method	142 $m^2\ g^{-1}$	0.1 M Na_2SO_4	709.8 Fg^{-1} at 0.2 A g^{-1}	97.6% after 1,000 cycles	2015	Wei et al. (2015b)
2	Coaxial mesoporous MnO_2/amorphous-carbon nanotubes	Redox reaction between $KMnO_4$ and amorphous carbon nanotube in acid solution	–	1 M Na_2SO_4	362 Fg^{-1} at the current density of 0.5 A g^{-1}	88.6% after 3,000 cycles	2015	Zhu et al. (2015)
3	3D porous CNT/ MnO_2 composite	Dipping and drying process followed by a potentionstatic deposition technology	230.85 $m^2\ g^{-1}$	0.5 M NaOH	160.5 Fg^{-1} at the current density of 1 A^{-1}	–	2015	Guo et al. (2015b)
4	Carbon nanosheets supported MnO_2	Carbonization and reduction method	573 $m^2\ g^{-1}$	6 M KOH	656 Fg^{-1} at a current density of 1 A g^{-1}	80% after 5,000 cycles	2015	Sun et al. (2015)
5	A RGO/manganese dioxide (MnO_2)/silver nanowire ternary hybrid film	A facile vacuum filtration and subsequent thermal reduction	–	0.5 M Na_2SO_4	4.42 F cm^{-3} at a scan rate of 10 mV s^{-1}	90.3% after 6,000 cycles	2015	Liu et al. (2015)
6	Three-dimensional carbon nanotubes@ MnO_2 core shell nanostructures	A floating catalyst chemical vapor deposition process and a facile hydrothermal approach	127.5 $m^2\ g^{-1}$	1 M Na_2SO_4	325.5 F g^{-1} at a current density of 0.3 A g^{-1}	90.5% after 5,000 cycles	2014	Huang et al. (2014b)
7	MnO_2/Graphine argogel composites	Graphene aerogels: an organic sol-gel process and MnO_2 electrochemically deposit on GA	793 $m^2\ g^{-1}$	0.5 M Na_2SO_4	410 Fg^{-1} at 2 mV s^{-1}	95% after 50,000 cycles at 1,000 mV s^{-1}	2014	Wang et al. (2014)
8	Manganese oxide nanosheets/ nanoporous gold	Galvanostatic electrodepositon	–	1 M Na_2SO_4	775 Fg^{-1} at 1 A g^{-1}	95% after 1,000 cycles	2015	Zeng et al. (2015)
9	MnO_2 on graphene	Hydrothermal method	–	1 M Na_2SO_4	315 Fg^{-1} at a current density of 0.2 A g^{-1}	87% retained after 2,000 cycles at 3 A g^{-1}	2013	Liu et al. (2013)
10	MnO_2 nanosheets on flexible carbon fiber cloth	Flexible carbon fiber cloth: the direct carbonization of flax textile redox reaction between carbon and $KMnO_4$	33.6 $m^2\ g^{-1}$	0.1 M Na_2SO_4	683.73 Fg^{-1} at 2 A g^{-1}	94.5% retained after 2,000 cycles	2015	He and Chen (2015)

use of new synthesis approaches, surface modifying agents, complexing, and structure directing agent results in high-specific capacitance, which is equal the theoretical specific capacitance cobalt oxide. In this review paper, we have focused the recent advancements in the cobalt oxides and their composites as the electrode material. **Table 1** shows the preparation and supercapacitive performance of cobalt oxide and their composites based supercapacitors.

RECENT ADVANCES IN MANGANESE OXIDE SUPERCAPACITOR

Manganese (Mn) has different oxidation states. Out of these, the most stable oxidation states are Mn (II) and Mn (IV). The Mn (II) forms MnO, on the other hand, Mn (IV) forms MnO_2 and Mn_2O_3. The MnO_2 has α, β, γ, and δ -type polymorph (Chen et al., 2014; Salunkhe et al., 2015). The advantages of manganese-based metal oxides include low cost, low toxicity, natural abundance, and environmental friendly in nature (Sui et al., 2015; Wei et al., 2015b). In aqueous and organic electrolyte, the MnO, MnO_2, and Mn_2O_3 can form the different oxidation states. Thus, it results in the high-specific capacitance. The highest reported theoretical specific capacitance of MnO_2 is 1.370 Fg^{-1} (Guo et al., 2015a; Wei et al., 2015b). However, the low electrical conductivity and large volume change during the charge–discharge process result in the unsatisfactory rate performance and cyclic stability. In consequence, this reduces the specific capacitance of the manganese oxides-based supercapacitors (Cabana et al., 2010; Chen et al., 2010). To overcome such hindrances, recently, the researchers have been executing many new strategies, such as use of carbon containing materials for increasing the electrical conductivity and adopt the volume buffers for relaxing internal stresses (Yao et al., 2008; Sui et al., 2015). Manganese oxides have been prepared by various synthesis methods, such as pulse laser deposition method (Xia et al., 2011), hydrothermal method (Zhang et al., 2014), electrochemical synthesis method (Jiang and Kucernak, 2002), redox deposition method (Bordjiba and Bélanger, 2009), successive hydrolysis–condensation method (Sawangphruk and Limtrakul, 2012), etc. Further, the detail of MnO_2 synthesis and their supercapacitive performance are shown in **Table 2**.

CONCLUSION AND FUTURE PROSPECTIVE

Recently, cobalt- and manganese-based metal oxide as the electrode materials for supercapacitor have been receiving the great attention. From the recent reports, it has concluded that,

(1) Advanced chemical method such as hydrothermal, pulse laser deposition, reverse microemulsion, microwave-assisted, etc., has been assisted to synthesize cobalt- and manganese-based metal oxide material.
(2) The specific capacitance of the cobalt oxide- and manganese-based metal oxide supercapacitor strongly depends on morphology, surface area, and pore-size distribution.
(3) In most of the reports, the composites of cobalt oxide or manganese oxide with carbon material, i.e., hybrid materials are used as an electrode for supercapacitor. Moreover, this results in high-specific capacitance.
(4) In addition, the increase in conductivity of the cobalt oxide and manganese oxides is projected if this material and carbon material are combined. This makes the application of cobalt oxide and manganese oxides in high energy applications. As a result, the proposed material cobalt oxides and manganese oxide are a promising material for flexible, portable high-rate hybrid supercapacitor, and has plenty room for advancements.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

FUNDING

This work is financially supported by University Grant Commission (UGC) New Delhi, India under Minor Research Project (File No.47-763/13/WRO).

REFERENCES

Adib, K., Rahimi-Nasrabadi, M., Rezvani, Z., Pourmortazavi, S. M., Ahmadi, F., Naderi, H. R., et al. (2016). Facile chemical synthesis of cobalt tungstates nanoparticles as high performance supercapacitor. *J. Mater. Sci. Mater. Electron.* 27, 4541. doi:10.1007/s10854-016-4329-4

Bordjiba, T., and Bélanger, D. (2009). Direct redox deposition of manganese oxide on multiscaled carbon nanotube/microfiber carbon electrode for electrochemical capacitor. *J. Electrochem. Soc.* 156, A378–A384. doi:10.1149/1.3090012

Cabana, J., Monconduit, L., Larcher, D., and Palacin, M. R. (2010). Beyond intercalation-based Li-Ion batteries: the state of the art and challenges of electrode materials reacting through conversion reactions. *Adv. Mater. Weinheim* 22, 35. doi:10.1002/adma.201000717

Chen, I. L., Chen, T. Y., Wei, Y. C., Hu, C. C., and Lin, T. L. (2014). Capacitive performance enhancements of RuO_2 nanocrystals through manipulation of preferential orientation growth originated from the synergy of Pluronic F127 trapping and annealing. *Nanoscale* 6, 2861–2871. doi:10.1039/c3nr04479c

Chen, S., Zhu, J., Wu, X., Han, Q., and Wang, X. (2010). Graphene oxide-MnO_2 nanocomposites for supercapacitors. *ACS Nano* 4, 2822–2830. doi:10.1021/nn901311t

Cheng, H., Lu, Z. G., Deng, J. Q., Chung, C. Y., Zhang, K., and Li, Y. Y. (2010). A facile method to improve the high rate capability of Co_3O_4 nanowire array electrodes. *Nano Res.* 3, 895–901. doi:10.1007/s12274-010-0063-z

Chodankar, N. R., Dubal, D. P., and Gund, G. S. (2015). Flexible all-solid-state MnO_2 thin films based symmetric supercapacitors. *Electrochim. Acta* 165, 338–347. doi:10.1016/j.electacta.2015.02.246

Deng, J., Kang, L., Bai, G., Li, Y., Li, P., Liu, X., et al. (2014). Solution combustion synthesis of cobalt oxides (Co_3O_4 and Co_3O_4/CoO) nanoparticles as supercapacitor electrode materials. *Electrochim. Acta* 132, 127–135. doi:10.1016/j.electacta.2014.03.158

Dubal, D. P., Kim, W. B., and Lokhande, C. D. (2012). Galvanostatically deposited Fe: MnO_2 electrodes for supercapacitor application. *J. Phys. Chem. Solids* 73, 18–24. doi:10.1016/j.jpcs.2011.09.005

Faraji, S., and Ani, F. N. (2015). The development supercapacitor from activated carbon by electroless plating – a review. *Renew. Sustain. Energ. Rev.* 42, 823–834. doi:10.1016/j.rser.2014.10.068

Guo, W. H., Liu, T. J., Jiang, P., and Zhang, Z. J. (2015a). Free-standing porous manganese dioxide/graphene composite films for high performance supercapacitors. *J. Colloid Interface Sci.* 437, 304–310. doi:10.1016/j.jcis.2014.08.060

Guo, C., Li, H., Zhang, X., Huo, H., and Xu, C. (2015b). 3D porous CNT/MnO_2 composite electrode for high-performance enzymeless glucose detection and supercapacitor application. *Sens. Actuators B Chem.* 206, 407–414. doi:10.1016/j.snb.2014.09.058

He, G., Li, J., Chen, H., Shi, J., Sun, X., Chen, S., et al. (2012). Hydrothermal preparation of Co_3O_4@ graphene nanocomposite for supercapacitor with enhanced capacitive performance. *Mater. Lett.* 82, 61. doi:10.1016/j.matlet.2012.05.048

He, S., and Chen, W. (2015). Application of biomass-derived flexible carbon cloth coated with MnO_2 nanosheets in supercapacitors. *J. Power Sources* 294, 150–158. doi:10.1016/j.jpowsour.2015.06.051

Hu, H., Guan, B., Xia, B., and Lou, X. W. (2015). Designed formation of Co_3O_4/$NiCo_2O_4$ double-shelled nanocages with enhanced pseudocapacitive and electrocatalytic properties. *J. Am. Chem. Soc.* 137, 5590–5595. doi:10.1021/jacs.5b02465

Huang, K. J., Wang, L., Zhang, J. Z., Wang, L. L., and Mo, Y. P. (2014a). One-step preparation of layered molybdenum disulfide/multi-walled carbon nanotube composites for enhanced performance supercapacitor. *Energy* 67, 234–240. doi:10.1016/j.energy.2013.12.051

Huang, M., Zhang, Y., Li, F., Zhang, L., Wen, Z., and Liu, Q. (2014b). Facile synthesis of hierarchical Co_3O_4@MnO_2 core-shell arrays on Ni foam for asymmetric supercapacitors. *J. Power Sources* 252, 98–106. doi:10.1016/j.jpowsour.2013.12.030

Jayalakshmi, M., and Balasubramanian, K. (2008). Simple capacitor to supercapacitor – an overview. *Int. J. Electrochem. Sci.* 11, 1196–1217.

Jiang, J., and Kucernak, A. (2002). Electrochemical supercapacitor material based on manganese oxide: preparation and characterization. *Electrochim. Acta* 47, 2381–2386. doi:10.1016/S0013-4686(02)00031-2

Kang, D., Liu, Q., Gu, J., Su, Y., Zhang, W., and Zhang, D. (2015). "Egg-box"-assisted fabrication of porous carbon with small mesopores for high-rate electric double layer capacitors. *ACS Nano* 9, 11225–11233. doi:10.1021/acsnano.5b04821

Kumar, R., Singh, R. K., Dubey, P. K., Singh, D. P., and Yadav, R. M. (2015). Self-assembled hierarchical formation of conjugated 3D cobalt oxide nanobead–CNT–graphene nanostructure using microwaves for high-performance supercapacitor electrode. *ACS Appl. Mater. Interfaces* 7, 15042–15051. doi:10.1021/acsami.5b04336

Lee, S. W., Gallant, B. M., Byon, H. R., Hammond, P. T., and Shao-Horn, Y. (2011). Nanostructured carbon-based electrodes: bridging the gap between thin-film lithium-ion batteries and electrochemical capacitors. *Energy Environ. Sci.* 4, 1972–1985. doi:10.1039/c0ee00642d

Liu, W., Lu, C., Wang, X., Tay, R. Y., and Tay, B. K. (2015). High-performance microsupercapacitors based on two-dimensional graphene/manganese dioxide/silver nanowire ternary hybrid film. *ACS Nano* 9, 1528–1542. doi:10.1021/nn5060442

Liu, X. Y., Gao, Y. Q., and Yang, G. W. (2016). A flexible, transparent and super-long-life supercapacitor based on ultrafine Co_3O_4 nanocrystal electrodes. *Nanoscale* 8, 4227–4235. doi:10.1039/C5NR09145D

Liu, Y., Yan, D., Zhuo, R., Li, S., Wu, Z., Wang, J., et al. (2013). Design, hydrothermal synthesis and electrochemical properties of porous birnessite-type manganese dioxide nanosheets on graphene as a hybrid material for supercapacitors. *J. Power Sources* 242, 78–85. doi:10.1016/j.jpowsour.2013.05.062

Liu, T., Kumar, S., Inventors; Georgia Tech Research Corporation, Assignee. (2006). *Supercapacitor Having Electrode Material Comprising Single-Wall Carbon Nanotubes and Process for Making the Same*. United States patent US 7,061,749.

Luo, Y., Zhang, H., Guo, D., Ma, J., Li, Q., Chen, L., et al. (2014). Porous $NiCo_2O_4$-reduced graphene oxide (rGO) composite with superior capacitance retention for supercapacitors. *Electrochim. Acta* 132, 332–337. doi:10.1016/j.electacta.2014.03.179

Madhu, R., Veeramani, V., Chen, S. M., Manikandan, A., Lo, A. Y., and Chueh, Y. L. (2015). Honeycomb-like porous carbon-cobalt oxide nanocomposite for high-performance enzymeless glucose sensor and supercapacitor applications. *ACS Appl. Mater. Interfaces* 7, 15812–15820. doi:10.1021/acsami.5b04132

Meher, S. K., and Rao, G. R. (2011). Effect of microwave on the nanowire morphology, optical, magnetic, and pseudocapacitance behavior of Co_3O_4. *J. Phys. Chem. C* 115, 25543–25556. doi:10.1021/jp209165v

Meng, C., Liu, C., Chen, L., Hu, C., and Fan, S. (2010). Highly flexible and all-solid-state paperlike polymer supercapacitors. *Nano Lett.* 10, 4025–4031. doi:10.1021/nl1019672

Pardieu, E., Pronkin, S., Dolci, M., Dintzer, T., Pichon, B. P., Begin, D., et al. (2015). Hybrid layer-by-layer composites based on a conducting polyelectrolyte and Fe_3O_4 nanostructures grafted onto graphene for supercapacitor application. *J. Mater. Chem. A* 3, 22877–22885. doi:10.1039/C5TA05132K

Ray, R. S., Sarma, B., Jurovitzki, A. L., and Misra, M. (2015). Fabrication and characterization of titania nanotube/cobalt sulfide supercapacitor electrode in various electrolytes. *Chem. Eng. J.* 260, 671–683. doi:10.1016/j.cej.2014.07.031

Salunkhe, R. R., Ahn, H., Kim, J. H., and Yamauchi, Y. (2015). Rational design of coaxial structured carbon nanotube–manganese oxide (CNT–MnO_2) for energy storage application. *Nanotechnology* 26, 204004. doi:10.1088/0957-4484/26/20/204004

Sarma, B., Ray, R. S., Mohanty, S. K., and Misra, M. (2014). Synergistic enhancement in the capacitance of nickel and cobalt based mixed oxide supercapacitor prepared by electrodeposition. *Appl. Surf. Sci.* 300, 29–36. doi:10.1016/j.apsusc.2014.01.186

Sawangphruk, M., and Limtrakul, J. (2012). Effects of pore diameters on the pseudocapacitive property of three-dimensionally ordered macroporous manganese oxide electrodes. *Mater. Lett.* 68, 230–233. doi:10.1016/j.matlet.2011.10.096

Shinde, S. K., Dubal, D. P., Ghodake, G. S., Gomez-Romero, P., Kim, S., and Fulari, V. J. (2015). Hierarchical 3D-flower-like CuO nanostructure on copper foil for supercapacitors. *RSC Adv.* 5, 30478–30484. doi:10.1039/C4RA11164H

Sui, Z. Y., Wang, C., Shu, K., Yang, Q. S., Ge, Y., Wallace, G. G., et al. (2015). Manganese dioxide-anchored three-dimensional nitrogen-doped graphene hybrid aerogels as excellent anode materials for lithium ion batteries. *J. Mater. Chem. A* 3, 10403–10412. doi:10.1039/C5TA05759K

Sun, K., Wang, H., Peng, H., Wu, Y., Ma, G., and Lei, Z. (2015). Manganese oxide nanorods supported on orange peel-based carbon nanosheets for high performance supercapacitors. *Int. J. Electrochem. Sci.* 10, 2000–2013.

Vijayakumar, S., Ponnalagi, A. K., Nagamuthu, S., and Muralidharan, G. (2013). Microwave assisted synthesis of Co_3O_4 nanoparticles for high-performance supercapacitors. *Electrochim. Acta* 106, 500–505. doi:10.1016/j.electacta.2013.05.121

Wang, C. C., Chen, H. C., and Lu, S. Y. (2014). Manganese oxide/graphene aerogel composites as an outstanding supercapacitor electrode material. *Chem. A Eur. J.* 20, 517–523. doi:10.1002/chem.201303483

Wang, G., Lu, X., Ling, Y., Zhai, T., Wang, H., Tong, Y., et al. (2012). LiCl/PVA gel electrolyte stabilizes vanadium oxide nanowire electrodes for pseudocapacitors. *ACS Nano* 6, 10296–10302. doi:10.1021/nn304178b

Wang, H. Q., Li, Z. S., Huang, Y. G., Li, Q. Y., and Wang, X. Y. (2010). A novel hybrid supercapacitor based on spherical activated carbon and spherical MnO_2 in a non-aqueous electrolyte. *J. Mater. Chem.* 20, 3883–3889. doi:10.1039/c000339e

Wei, H., He, C., Liu, J., Gu, H., Wang, Y., Yan, X., et al. (2015a). Electropolymerized polypyrrole nanocomposites with cobalt oxide coated on carbon paper for electrochemical energy storage. *Polymer* 67, 192–199. doi:10.1016/j.polymer.2015.04.064

Wei, B., Wang, L., Miao, Q., Yuan, Y., Dong, P., Vajtai, R., et al. (2015b). Fabrication of manganese oxide/three-dimensional reduced graphene oxide composites as the supercapacitors by a reverse microemulsion method. *Carbon N. Y.* 85, 249–260. doi:10.1016/j.carbon.2014.12.063

Xia, X. H., Tu, J. P., Zhang, Y. Q., Mai, Y. J., Wang, X. L., Gu, C. D., et al. (2011). Three-dimentional porous nano-Ni/Co$(OH)_2$ nanoflake composite film: a pseudocapacitive material with superior performance. *J. Phys. Chem. C* 115, 22662–22668. doi:10.1021/jp208113j

Xu, J., Gao, L., Cao, J., Wang, W., and Chen, Z. (2010). Preparation and electrochemical capacitance of cobalt oxide (Co_3O_4) nanotubes as supercapacitor material. *Electrochim. Acta* 56, 732–736. doi:10.1016/j.electacta.2010.09.092

Yang, W., Gao, Z., Ma, J., Wang, J., Wang, B., and Liu, L. (2013). Effects of solvent on the morphology of nanostructured Co_3O_4 and its application for high-performance supercapacitors. *Electrochim. Acta* 112, 378–385. doi:10.1016/j.electacta.2013.08.056

Yao, W. L., Wang, J. L., Yang, J., and Du, G. D. (2008). Novel carbon nanofiber-cobalt oxide composites for lithium storage with large capacity and high reversibility. *J. Power Sources* 176, 369–372. doi:10.1016/j.jpowsour.2007.10.073

Yu, G., Xie, X., Pan, L., Bao, Z., and Cui, Y. (2013). Hybrid nanostructured materials for high-performance electrochemical capacitors. *Nano Energy* 2, 213–234. doi:10.1016/j.nanoen.2012.10.006

Yu, Z. J., Dai, Y., and Chen, W. (2009). Synthesis of Co_2O_4 microspheres by hydrothermal-precipitation for electrochemical supercapacitors. *Adv. Mater. Res.* 66, 280–283. doi:10.4028/www.scientific.net/AMR.66.280

Zeng, Z., Zhou, H., Long, X., Guo, E., and Wang, X. (2015). Electrodeposition of hierarchical manganese oxide on metal nanoparticles decorated nanoporous gold with enhanced supercapacitor performance. *J. Alloys Comp.* 632, 376–385. doi:10.1016/j.jallcom.2015.01.240

Zhang, F., Zhang, T., Yang, X., Zhang, L., Leng, K., Huang, Y., et al. (2013). A high-performance supercapacitor-battery hybrid energy storage device based on graphene-enhanced electrode materials with ultrahigh energy density. *Energy Environ. Sci.* 6, 1623–1632. doi:10.1039/c3ee40509e

Zhang, J., and Zhao, X. S. (2012). Conducting polymers directly coated on reduced graphene oxide sheets as high-performance supercapacitor electrodes. *J. Phys. Chem. C* 116, 5420–5426. doi:10.1021/jp211474e

Zhang, X., Sun, X., Zhang, H., Li, C., and Ma, Y. (2014). Comparative performance of birnessite-type MnO_2 nanoplates and octahedral molecular sieve (OMS-5) nanobelts of manganese dioxide as electrode materials for supercapacitor application. *Electrochim. Acta* 132, 315–322. doi:10.1016/j.electacta.2014.03.176

Zhu, S. J., Zhang, J., Ma, J. J., Zhang, Y. X., and Yao, K. X. (2015). Rational design of coaxial mesoporous birnessite manganese dioxide/amorphous-carbon nanotubes arrays for advanced asymmetric supercapacitors. *J. Power Sources* 278, 555–561. doi:10.1016/j.jpowsour.2014.12.054

Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.