Chapter

Graphene-Based Materials for Supercapacitor

Abu Jahid Akhtar

Abstract

Graphene, a one-atomic-thick film of two-dimensional nanostructure, has piqued the attention of researchers due to its superior electrical conductivity, large surface area, good chemical stability, and excellent mechanical behaviour. These extraordinary properties make graphene an appropriate contender for energy storage applications. However, the agglomeration and re-stacking of graphene layers due to the enormous interlayer van der Waals attractions have severely hampered the performance of supercapacitors. Several strategies have been introduced to overcome the limitations and established graphene as an ideal candidate for supercapacitor. The combination of conducting polymer (CP) or metal oxide (MO) with graphene as electrode material is expected to boost the performance of supercapacitors. Recent reports on various CP/graphene composites and MO/graphene composites as supercapacitor electrode materials are summarised in this chapter, with a focus on the two basic supercapacitor mechanisms (EDLCs and pseudocapacitors).

Keywords: Supercapacitor, EDLC, Pseudo-capacitance, Metal oxides, Conducting polymers

1. Introduction

Energy storage devices are important in today's world to meet the increasing demand for reliable and portable power sources [1–3]. Supercapacitors, also known as ultracapacitors, are electrochemical energy storage devices that are lightweight, can operate at a wide range of temperatures, have a long life cycle, and are shielded to make their work easier [4, 5]. With a number of such advantages, the supercapacitors emerged in a variety of applications in hybrid or electric vehicles, electronics and aircrafts [4, 5]. Today, supercapacitor manufacturers mostly use coconut activated carbon as an electrode material due to its high specific surface area, low price and mass production capability. However, with increased energy demand, significant research efforts have been made to find ideal electrode materials for the production of advanced energy storage systems. Energy is stored in supercapacitors via two energy storage mechanism, namely electrochemical double layer capacitance (EDLC) and pseudocapacitance. So, in order to improve supercapacitor efficiency, both of these mechanisms must be incorporated on a single electrode material.

Graphene, a one-atom-thick 2D single layer of sp^2 -bonded carbon atoms with the hexagonal lattice structure, is considered as the basic building block material for all carbon materials [6, 7]. Graphene has emerged as an appropriate candidate for energy storage applications due to its high electrical (10^8 S/m) and thermal conductivity (5000 W/m/K), large surface area ($2.63X10^6 m^2/kg$), high transparency (absorbance of 2.3%), good chemical stability, and excellent mechanical behaviour (breaking strength of 42 N/m and Young's modulus of 1.0 TPa) [8, 9]. Various methods such as chemical vapour deposition (CVD) of hydrocarbons, epitaxial growth on electrically insulating surfaces such as SiC, micromechanical exfoliation of graphite (Scotch tape method), oxidation–exfoliation–reduction of graphite powder may be used to synthesise graphene sheets of various sizes and defect contents [10]. Among these methods, graphene sheet which is grown by chemical vapour deposition (CVD) of hydrocarbon [11] has the superior quality with minimal defects. However, CVD prepared graphene would not be an ideal contender for EDLC electrode material, as it is too costly to produce and is hardly scalable. On the other hand, graphene produced by a chemical or thermal exfoliation process [12] of graphite is relatively inexpensive but has more surface defects which prevent graphene from being used in high-speed electronic, photonic/optoelectronic devices. But these defects play an important role in supercapacitor applications. So graphene with defects is used as an acceptable supercapacitor material. However, due to the large interlayer van der Waals attractions, re-stacking of graphene layers can severely reduce the available electrochemical surfaces, obstructing ion diffusion and ultimately limiting electrochemical efficiency, and the lack of fast Faradic pseudocapacitive behaviour have severely hampered supercapacitor performance. In order to address the issue graphene is often combined with other materials such as different metal oxides (MP) and conducting polymers (CP) to further increase its electrochemical performance. Coupling MPs or CPs to graphene has been shown to be an effective approach to improving the cycling stability, energy and power density of the supercapacitor device by introducing pseudocapacitance [13–37]. This chapter summarises recent studies on various CP/graphene composites and MO/graphene composites as supercapacitor electrode materials, with an emphasis on the two basic supercapacitor mechanisms (EDLCs and pseudocapacitors).

2. Graphene-metal oxide nanocomposites for supercapacitor applications

Metal oxide supercapacitors have gotten a lot of attention in recent years because of their high theoretical basic capacitance, low cost, environmental friendliness, and natural abundance [38–45]. Metal oxides also allow rapid, reversible faradic reactions to the electrode-electrolyte interface [46] resulting in large specific capacitances. However, the power density and cycling stability of the metal oxide based supercapacitor device are limited by poor electronic and ionic conductivity of metal oxides. So metal oxides are often combined with graphene to address these drawbacks, and it is expected that hybrid metal oxide/graphene nanostructures can increase supercapacitor performance for large-scale energy storage systems.

2.1 Graphene-manganese oxide nanocomposites

Manganese oxide-graphene composite is the most studied electrode material for supercapacitor devices among metal oxides [13–15]. The charge storage mechanism of a MnO2 electrode involves a transition in manganese (Mn) oxidation state from III to IV. The reversible insertion/extraction of electrolyte cations to balance the charge during reduction/oxidation of Mn^{+3}/Mn^{+4} gives MnO2 its pseudocapacitive properties [47, 48].

He et al. [13] used electrodeposition to build freestanding, lightweight (0.75 mg/cm^2), ultrathin (<200 μm), highly conductive (55 S/cm), and flexible three-dimensional (3D) graphene networks filled with MnO_2 as the flexible supercapacitor electrode material. The composite with 9.8 mg/cm^2 MnO_2mass loading (92.9% of the total electrode mass) had a capacitance of 1.42 F/cm^2 in a scan rate of 2 mV/s. He et al. further optimised the MnO_2 content in the composite material for realistic applications and achieved a maximum specific capacitance of 130 F/g.

Another research [14] rendered graphene/ MnO_2 composites by chemically reducing GO/ MnO_2 with both hydrazine hydrate (H-RGO/MnO_2) and sodium borohydride (S-RGO/ MnO_2) as reducing agents. The H-RGO/MnO_2 showed a specific capacitance of 327.5 F/g, which is higher than that of the S-RGO/MnO_2 (278.6 F/g). Kim et al. proposed that using the hydrazine reduction process to fabricate MnO_2 on graphene oxide surfaces is a promising fabrication method for supercapacitor electrodes.

For producing highly efficient graphene/metal oxide-based hybrid supercapacitors, Wang et al. [15] described in situ synthesis of 3D-graphene/MnO2 foam composite using a combination of chemical vapour deposition and hydrothermal process. High crystallinity and low contact resistance were observed during in situ conformal growth of 3D-graphene/MnO_2 composites. In the supercapacitor, the 3D-graphene/MnO_2 composite electrode demonstrated high specific capacitance (333.4 F/g at 0.2 A/g) and excellent cycling stability (92.2% retention at 0.2 A/g after 2000 cycles).

Thus these methods for fabricating graphene/MnO_2 composites offers a promising means of producing energy storage electrode materials for supercapacitor devices with high efficiency.

2.2 Graphene-iron oxide nanocomposites

Iron oxides drew interest as a potential electrode material due to their natural abundance, high thermal stability, and low toxicity [42, 43]. However, in terms of power density and cyclic stability, iron oxide struggles as an electrode material and must be combined with graphene to overcome the problem.

Reduced graphene oxide- Fe_3O_4 (RGO-Fe_3O_4) nanocomposite was synthesised by Ghasemi and co-worker [16] using a simple electrophoretic deposition (EPD) method followed by an electrochemical reduction procedure. On RGO, Fe_3O_4 nanoparticles with a diameter of 20–50 nm are uniformly assembled. At a current density of 1 A/g, RGO- Fe_3O_4 had a specific capacitance of 154 F/g, which is greater than RGO (81 F/g) in Na_2SO_4 electrolyte. The electrochemical behaviours of this study also revealed that adding surfactant to aqueous Na_2SO_4 solution would boost the capacitance of RGO- Fe_3O_4 electrodes. RGO- Fe_3O_4 electrode in Na2SO4 electrolyte containing t-octyl phenoxy polyethoxyethanol (Triton X-100) showed capacitance of 236 F/g at 1 A/g, with 97% of the initial capacitance retained after 500 cycles.

Qu et al. [17] have shown that the increase in electrochemical capacitive performance of 2D Fe_3O_4 -graphene nanocomposites was mainly due to the optimization of electrochemical surfaces by avoiding graphene re-stacking due to the uniform Fe_3O_4 surface deposition and synergistic effect of Fe_3O_4 and graphene. The hybrid capacitor shows a capacitance value of 304 F/g. In addition, Fe_3O_4 -graphene nanocomposites have achieved higher power density.

In another work Tang et al. [18] synthesised three-dimensional (3D) iron oxide/graphene aerogel hybrid using an innovative in situ hydrothermal process for supercapacitor applications. This material Fe_2O_3/GA hybrid electrode were used to make a highly flexible all-solid-state symmetric supercapacitor system.

The device provided a high specific capacity of 440 F/g and was suitable for different bending angles. 90% of the capacitance was also preserved after 2200 cycles, indicating strong cycling stability. These excellent electrochemical performances suggest that graphene-iron oxide nanocomposites have huge potential in energy application.

2.3 Graphene-nickel oxide nanocomposites

Nickel oxide (NiO) has been shown to be one of the most promising electrode materials for supercapacitors [38, 39]. However, the efficacy of NiO has been found to be reduced due to its low electrical conductivity, resulting in poor performance in electrochemical devices. Researchers are trying to boost its efficiency by linking it to graphene.

A simple solvothermal-induced self-assembly method was used by Gui and co-worker [19] to make three-dimensional nickel oxide/graphene aerogel nanocomposites (NiO/GA). With an extremely large working potential window, the NiO/GA electrodes attained a specific capacitance of 587.3 F/g at 1A/g. The NiO/GA had excellent cycling reliability, with only a minor decrease in capacitance after 1000 cycles.

Zhao et al. [20] demonstrated NiO's electrochemical properties by growing NiO mesoporous nanowalls on rGO nanosheets on 3D nickel foams, referring to the process as binder-free electrode preparation. The NiO-graphene nanocomposite 3D porous foam composite substrate offers an appropriate structure for electron collection and electrolyte/ion diffusion via the active materials, resulting in a high specific capacitance of 950 F/g at a current density of 5 A/g with excellent cycling stability.

In another work Choi et al. [21] demonstrated the synthesis of 3D porous graphene/NiO nanoparticle composites (3D-RGNi) by a facile method. The prepared 3D-RGNi had a large electrochemically active surface region. The as-synthesised 3D-RGNi electrode had a large specific capacitance of 1328 F/g at 1A/g and superb rate capability, with 87% of the capacitance retained after 2000 cycles. The synergistic effects of the rGO network and NiO nanoparticles, as well as the highly porous structure of 3D-RGNi, are attributed with these high capacitance results.

Hence, it is expected that graphene-Nickel oxide nanocomposites might serve as a favourable materials for energy storage applications.

2.4 Graphene-cobalt oxide nanocomposites

Apart from having a high theoretical capacitance (3560 F/g) and being abundant in nature, cobalt-oxide based nanomaterials are also said to be environmentally friendly [49, 50]. The faradaic redox transitions of interfacial oxy-cation species trigger the pseudo capacitance of hydrous Cobalt oxides [51]. The formation of cobalt oxide phases with a transition between Co(II), Co(III), and Co(IV) oxidation states explains the charge–discharge process of cobalt oxide in alkaline electrolyte.

Akhtar et al. [22] presented the preparation of nanostructured cobalt oxide/reduced graphene oxide (Co_3O_4/rGO) composites for potential materials in supercapacitor applications using a basic one-step cost-effective hydrothermal technique. The v nanoparticles in the Co_3O_4/rGO nanocomposites were layered over the surface of the rGO sheets. In a three electrode cell system, Co_3O_4/rGO nanocomposite based electrode had a specific capacitance of 754 F/g and after 1000 continuous cycles, the material abled to maintained 96% of its initial capability.

Chen et al. [23] used a simple hydrothermal technique to manufacture cobalt oxide (Co_3O_4) nanowires on three-dimensional (3D) graphene foam. The free-standing electrode for supercapacitor application was prepared from the synthesised 3D graphene/Co_3O_4 composite. It showed a high specific capacitance of 1100 F/g and excellent cycling stability at a current density of 10 A/g.

3. Graphene-conducting polymers for supercapacitor applications

Conducting polymers (CPs) attains lots of attention in academia and industry as electrode materials for supercapacitor. Polyaniline (PANI), polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) are type of conducting polymers [34, 52–56] that are extensively studied for supercapacitor device by offering very fast redox reaction with an electrolyte which can lead to pseudo-capacitance. However, CPs have a disadvantage of long-term stability due to the mechanical degradation of CPs. Thus graphene is often used to overcome the issue with CPs and guide to long term cycling stability, which is vital for supercapacitor devices.

3.1 Graphene- polyaniline (PANI) composite

PANI exhibit excellent conductivity and stability and have been widely used in energy storage devices [52, 53]. During the last few years, graphene/PANI composite nanocomposites have been used as electrode materials for supercapacitors [24–28]. Wu et al. [24] demonstrated synthesis of polyaniline nanofiber on graphene by in situ polymerisation of aniline monomer in the presence of graphene oxide under acid condition. The supercapacitor devices shows a specific capacitance of 480 F/g at a current density of 0.1 A/g and the material retained 70% of the original capacitance value after 1000 cycles. Gomes et al. [25] aimed to improve the cyclic stability by preparing hierarchical assembly of graphene/polyaniline nanostructures by microemulsion polymerisation, followed by the incorporation of graphene oxide nanosheets by hierarchical organisation. Hierarchical nanostructures showed a specific capacitance of 448F/g which is almost double of that of PANI due to the synergistic combination of graphene and PANI nanostructures. At the same time almost 81% capacity retention was achieved for the material compared to 38% for PANI after 5000 cyclic operations. Cheng et al. [26] prepared graphene–PANI composite paper as a flexible electrode, by combining the advantages of high conductivity, mechanical strength, and flexibility of graphene paper and large capacitance of the PANI. Based on these properties, this flexible graphene–PANI electrode material displayed a good tensile strength of 12.6 MPa and a stable large electrochemical capacitance of 233 F/g and 135 F/cm3 for gravimetric and volumetric capacitances, respectively.

Zhang et al. [27] reported a novel method to prepare flexible graphene/polyaniline paper (GPp) as supercapacitor electrodes through controlled in-situ polymerisation followed by roll coating in order to increase the electrochemical properties. This GPp deliver a high specific capacitance of 838 F/g at a current density of 1 A/g and high retention of 93.7% at 10 A/g over 5000 cycles. Kinetics analysis of the material shows that the GPp stores both surface capacitance and diffusion capacitance. The as-prepared GPp also showed a specific energy density as high as 40 Wh/kg and a power density of 10 kW/kg. The authors also succeeded to light the light emitting diode (LED) connected with the fabricated GPp device.

Another method which is commonly used for the preparation of graphene polymer composite is physical mixing in a given solvent. Flexible Graphene/Polyaniline Nanofiber Composite films were prepared by vacuum filtration of the mixed dispersions of both rGO and PANI nanofibers. [28] The film was mechanically stable and showed a good flexibility. The supercapacitor devices showed large electrochemical capacitance of 210 F/g at a low discharge rate of 0.3 A/g.

3.2 Graphene-Polypyrrole (PPy)

PPy is emerged as attracting material for supercapacitor [54, 55] because of its simple synthesis procedure and it has good thermal and electrical conductivity. However, the thin PPy film forms aggregated a cauliflower-like structure which is not favourable for supercapacitor applications. In order to address the issue PPy is often combined with graphene to improve its electrochemical performance. Zhang et al. [29] synthesised graphene and polypyrrole composite via in situ polymerisation of pyrrole monomer in the presence of graphene under acid conditions An even composite is formed with polypyrrole being uniformly bounded by graphene sheets. Electrochemical performance of the composite material are higher than pure samples with the maximum capacitance of 482 F/g and excellent cycling performance (95% retention after 1000 cycles). Liu et al. [30] demonstrated preparation of hierarchical graphene/polypyrrole nanocomposites via in-situ polymerisation of self-assembled pyrrole. The nanomaterial attained outstanding conductivity of ~1980 S/cm and demonstrated promising potential in supercapacitor, with a specific capacitance value 650 F/g at 0.45 A/g current density. Furthermore, the device showed energy density of 54.0 W h/kg at 1 mA current, and power density of 778.1 W/kg at 5 mA current. In another work Akhtar et al. [31] studied the electrochemical performance of graphene/polypyrrole layered type structure. Charge transport was investigated in this study to determine the relative contributions of graphene and polypyrrole in charge transport and storage mechanism, with the aim of improving device properties. Electrochemical supercapacitor fabricated using this layered composite exhibited a large value (~931 F/g) of specific capacitance.

3.3 Graphene/(PEDOT:PSS) composite

PEDOT: PSS attract as one of the potential electrode materials due to its good electrical conductivity, transparency, ductility, and stability [34, 56]. Wu et al. [32] demonstrated ultrathin printable graphene supercapacitors based on solution-processed electrochemically exfoliated graphene hybrid films on an ultrathin poly(ethylene terephthalate) substrate. The device exhibited an unprecedented volumetric capacitance of 348 F/cm3 at an ultrahigh scan rate of 2000 V/s, and AC line-filtering performance. This method can be possibly used for large-scale production of printable, thin and lightweight supercapacitor devices.

Fibre-shaped supercapacitors [33] with high mechanical and electronic properties based on hollow rGO/PEDOT: PSS (HCF) have gained tremendous attention because of their tiny volume, low weight, high flexibility, and good wearability. This novel fibre-shaped supercapacitor showed a high specific capacitance of 304.5 mF/cm2 at 0.08 mA/cm2 and an energy density of 27.1 mWh/cm2. In another work highly flexible, bendable and conductive rGO-PEDOT/PSS films were prepared by Chen et al. [34] The assembled device could be bent and twisted without harming the electrochemical performance of the device. A high areal capacitance of 448 mF/cm2 was achieved at a scan rate of 10 mV/s and when the device was fully charged the device was powerful enough to power a LED for 20 seconds.

3.4 Graphene/other polymers composite

Besides the above-mentioned conducting polymers there are others polymers that have been combined with graphene for supercapacitor devices. Gupta and co-workers [35] synthesised Poly (3-hexylthiophene)/graphene composites via both in-situ and ex-situ growth technique to investigate supercapacitive behaviour. They observed that in-situ growth of P3HT forms better composites with graphene than ex-situ growth. The values of specific capacitance for ex-situ and in-situ samples were found to be 244 F/g and 323 F/g respectively at a current density of 200 mA/g. Thus in-situ P3HT/graphene composite showed superior storage capacity in comparision to ex-situ sample. Electrochemical performance was also studied for graphene (G)–polyethylenedioxythiophene (PEDOT) nanocomposites as electrode material [36]. This manuscript presented the capacitance studies on supercapacitor G-PEDOT electrode with respect to stability of material, specific capacitance and electrical conductivity. Specific capacitance value for G-PEDOT sample was estimated to be 374 F/g. Wu et al. [37] reported conjugated polyfluorene imidazolium ionic liquids (coPIL) intercalated reduced graphene oxide (coPIL-RGO) for high performance supercapacitor. coPIL-RGO based device showed a specific capacitance of 222 F/g at a low current density of 0.2 A/g in 6 M KOH and 132 F/g at a current density of 0.5 A/g in ionic liquid electrolyte 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF4), respectively.

4. Conclusion

Metal oxide and Conducting polymers have gotten a lot of attention in next-generation supercapacitor electrode research because of their simple synthesis procedure, low cost and high pseudocapacitance. Simultaneously, pure metal oxide and conducting polymers have a number of flaws, including low electrical conductivity, weak cyclic stability, and low energy and power density. Graphene/conducting polymer composites and graphene/metal oxide composites outperform conducting polymers and metal oxides in terms of cyclic durability, energy density, and power density. Simultaneously, in recent years, considerable focus has been placed on structural architecture, material fabrication, and device performance evaluation. To accomplish the expected full-scale realistic application, both the efficiency and reproducible quantity of the electrode materials must be improved in the immediate future.

Author details

Abu Jahid Akhtar
Department of Physics, Diamond Harbour Women's University, West Bengal, India

*Address all correspondence to: jahid.dhwu@gmail.com

References

[1] Dell RM, Rand DAJ. Energy storage—a key technology for global energy sustainability. Journal of power sources. 2001; 100: 2-17.

[2] Suberu MY, Mustafa MW, Bashir N. Energy storage systems for renewable energy power sector integration and mitigation of intermittency. Renewable Sustainable Energy Reviews. 2014; 35: 499-514.

[3] Yoo HD, Markevich E, Salitra G, Sharon D, Aurbach D. On the challenge of developing advanced technologies for electrochemical energy storage and conversion. Materials Today. 2014; 17: 110-121.

[4] Raza W, Ali F, Raza N, Luo Y, Kim K-H, Yang J, Kumar S, Mehmood A, Kwon EE. Recent advancements in supercapacitor technology. Nano Energy. 2018; 52: 441-473.

[5] Zuo W, Li R, Zhou C, Li Y, Xia J, Liu J. Battery-supercapacitor hybrid devices: recent progress and future prospects. Advanced science. 2017; 4: 1600539.

[6] Dong Y, Wu Z-S, Ren W, Cheng H-M, Bao X. Graphene: a promising 2D material for electrochemical energy storage. Science Bulletin. 2017; 62: 724-740.

[7] Mas-Balleste R, Gomez-Navarro C, Gomez-Herrero J, Zamora F. 2D materials: to graphene and beyond. Nanoscale. 2011; 3: 20-30.

[8] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA. Electric field effect in atomically thin carbon films. science. 2004; 306: 666-669.

[9] Geim AK, Novoselov KS. The rise of graphene. Nature Materials 2007; 6: 183-191.

[10] Choi W, Lahiri I, Seelaboyina R, Kang YS. Synthesis of graphene and its applications: a review. Critical Reviews in Solid State Materials Sciences. 2010; 35: 52-71.

[11] Li X, Cai W, Colombo L, Ruoff RS. Evolution of graphene growth on Ni and Cu by carbon isotope labeling. Nano letters. 2009; 9: 4268-4272.

[12] Yu H, Zhang B, Bulin C, Li R, Xing R. High-efficient synthesis of graphene oxide based on improved hummers method. Scientific reports. 2016; 6: 1-7.

[13] He Y, Chen W, Li X, Zhang Z, Fu J, Zhao C, Xie E. Freestanding three-dimensional graphene/MnO2 composite networks as ultralight and flexible supercapacitor electrodes. ACS nano. 2013; 7: 174-182.

[14] Kim M, Hwang Y, Kim J. Graphene/MnO2-based composites reduced via different chemical agents for supercapacitors. Journal of power sources. 2013; 239: 225-233.

[15] Bai X-L, Gao Y-L, Gao Z-Y, Ma J-Y, Tong X-L, Sun H-B, Wang JA. Supercapacitor performance of 3D-graphene/MnO2 foam synthesized via the combination of chemical vapor deposition with hydrothermal method. Applied Physics Letters. 2020; 117: 183901.

[16] Ghasemi S, Ahmadi F. Effect of surfactant on the electrochemical performance of graphene/iron oxide electrode for supercapacitor. Journal of Power Sources. 2015; 289: 129-137.

[17] Qu Q, Yang S, Feng X. 2d sandwich-like sheets of iron oxide grown on graphene as high energy anode material for supercapacitors. Advanced materials. 2011; 23: 5574-5580.

[18] Khattak AM, Yin H, Ghazi ZA, Liang B, Iqbal A, Khan NA, Gao Y, Li L, Tang Z. Three dimensional iron oxide/graphene aerogel hybrids as all-solid-state flexible supercapacitor electrodes. RSC advances. 2016; 6: 58994-59000.

[19] Chen W, Gui D, Liu J. Nickel oxide/graphene aerogel nanocomposite as a supercapacitor electrode material with extremely wide working potential window. Electrochimica Acta. 2016; 222: 1424-1429.

[20] Zhao B, Wang T, Jiang L, Zhang K, Yuen MM, Xu J-B, Fu X-Z, Sun R, Wong C-P. NiO mesoporous nanowalls grown on RGO coated nickel foam as high performance electrodes for supercapacitors and biosensors. Electrochimica Acta. 2016; 192: 205-215.

[21] Trung NB, Van Tam T, Dang DK, Babu KF, Kim EJ, Kim J, Choi WM. Facile synthesis of three-dimensional graphene/nickel oxide nanoparticles composites for high performance supercapacitor electrodes. Chemical Engineering Journal. 2015; 264: 603-609.

[22] Sagadevan S, Marlinda AR, Johan MR, Umar A, Fouad H, Alothman OY, Khaled U, Akhtar M, Shahid M. Reduced graphene/nanostructured cobalt oxide nanocomposite for enhanced electrochemical performance of supercapacitor applications. Journal of colloid interface science. 2020; 558: 68-77.

[23] Dong X-C, Xu H, Wang X-W, Huang Y-X, Chan-Park MB, Zhang H, Wang L-H, Huang W, Chen P. 3D graphene–cobalt oxide electrode for high-performance supercapacitor and enzymeless glucose detection. ACS nano. 2012; 6: 3206-3213.

[24] Zhang K, Zhang LL, Zhao X, Wu J. Graphene/polyaniline nanofiber composites as supercapacitor electrodes. Chemistry of Materials. 2010; 22: 1392-1401.

[25] Hassan M, Reddy KR, Haque E, Faisal SN, Ghasemi S, Minett AI, Gomes VG. Hierarchical assembly of graphene/polyaniline nanostructures to synthesize free-standing supercapacitor electrode. Composites science technology. 2014; 98: 1-8.

[26] Wang D-W, Li F, Zhao J, Ren W, Chen Z-G, Tan J, Wu Z-S, Gentle I, Lu GQ, Cheng H-M. Fabrication of graphene/polyaniline composite paper via in situ anodic electropolymerization for high-performance flexible electrode. ACS nano. 2009; 3: 1745-1752.

[27] Yu H, Ge X, Bulin C, Xing R, Li R, Xin G, Zhang B. Facile fabrication and energy storage analysis of graphene/PANI paper electrodes for super capacitor application. Electro chimica Acta. 2017; 253: 239-247.

[28] Wu Q, Xu Y, Yao Z, Liu A, Shi G. Supercapacitors based on flexible graphene/polyaniline nanofiber composite films. ACS nano. 2010; 4: 1963-1970.

[29] Zhang D, Zhang X, Chen Y, Yu P, Wang C, Ma Y. Enhanced capacitance and rate capability of graphene/polypyrrole composite as electrode material for supercapacitors. Journal of Power Sources. 2011; 196: 5990-5996.

[30] Liu Y, Wang H, Zhou J, Bian L, Zhu E, Hai J, Tang J, Tang W. Graphene/polypyrrole intercalating nano composites as supercapacitors electrode. Electrochimica Acta. 2013; 112: 44-52.

[31] Akhtar AJ, Mishra S, Saha SK. Charge transport mechanism in reduced graphene oxide/polypyrrole based ultrahigh energy density supercapacitor. Journal of Materials Science: Materials in Electronics. 2020; 31: 11637-11645.

[32] Wu ZS, Liu Z, Parvez K, Feng X, Müllen K. Ultrathin printable graphene supercapacitors with AC line-filtering performance. Advanced Materials. 2015; 27: 3669-3675.

[33] Qu G, Cheng J, Li X, Yuan D, Chen P, Chen X, Wang B, Peng H. A fiber supercapacitor with high energy density based on hollow graphene/conducting polymer fiber electrode. Advanced materials. 2016; 28: 3646-3652.

[34] Liu Y, Weng B, Razal JM, Xu Q, Zhao C, Hou Y, Seyedin S, Jalili R, Wallace GG, Chen J. High-performance flexible all-solid-state supercapacitor from large free-standing graphene-PEDOT/PSS films. Scientific reports. 2015; 5: 1-11.

[35] Gupta A, Akhtar AJ, Saha SK. In-situ growth of P3HT/graphene composites for supercapacitor application. Materials Chemistry Physics. 2013; 140: 616-621.

[36] Alvi F, Ram MK, Basnayaka PA, Stefanakos E, Goswami Y, Kumar A. Graphene–polyethylenedioxythiophene conducting polymer nanocomposite based supercapacitor. Electrochimica Acta. 2011; 56: 9406-9412.

[37] Kötz R, Carlen M. Principles and applications of electrochemical capacitors. Electrochimica acta. 2000; 45: 2483-2498.

[38] Zheng Y-z, Ding H-y, Zhang M-l. Preparation and electrochemical properties of nickel oxide as a supercapacitor electrode material. Materials Research Bulletin. 2009; 44: 403-407.

[39] Vidhyadharan B, Zain NKM, Misnon II, Abd Aziz R, Ismail J, Yusoff MM, Jose RJ. High performance supercapacitor electrodes from electrospun nickel oxide nanowires. Journal of Alloys Compounds. 2014; 610: 143-150.

[40] Kandalkar SG, Gunjakar J, Lokhande C. Preparation of cobalt oxide thin films and its use in supercapacitor application. Applied Surface Science. 2008; 254: 5540-5544.

[41] Xu J, Gao L, Cao J, Wang W, Chen Z. Preparation and electrochemical capacitance of cobalt oxide (Co3O4) nanotubes as supercapacitor material. Electrochimica Acta. 2010; 56: 732-736.

[42] Mitchell E, Gupta RK, Mensah-Darkwa K, Kumar D, Ramasamy K, Gupta BK, Kahol P. Facile synthesis and morphogenesis of superparamagnetic iron oxide nanoparticles for high-performance supercapacitor applications. New Journal of Chemistry. 2014; 38: 4344-4350.

[43] Kulal PM, Dubal DP, Lokhande CD, Fulari VJ. Chemical synthesis of Fe2O3 thin films for supercapacitor application. Journal of Alloys Compounds. 2011; 509: 2567-2571.

[44] Yu Z, Duong B, Abbitt D, Thomas J. Highly ordered MnO2 nanopillars for enhanced supercapacitor performance. Advanced materials. 2013; 25: 3302-3306.

[45] Wang P, Zhao Y-J, Wen L-X, Chen J-F, Lei Z-G. Ultrasound–microwave-assisted synthesis of MnO2 supercapacitor electrode materials. Industrial Engineering Chemistry Research. 2014; 53: 20116-20123.

[46] Lang X, Hirata A, Fujita T, Chen M. Nanoporous metal/oxide hybrid electrodes for electrochemical supercapacitors. Nature nanotechnology. 2011; 6: 232-236.

[47] Kuo S-L, Wu N-L. Investigation of pseudocapacitive charge-storage reaction of MnO2• nH2O supercapacitors in aqueous electrolytes. Journal of The Electrochemical Society. 2006; 153: A1317.

[48] Kozawa A, Powers R. The Manganese Dioxide Electrode in Alkaline Electrolyte; The Electron-Proton Mechanism for the Discharge Process from MnO2 to MnO1. 5. Journal of The Electrochemical Society. 1966; 113: 870.

[49] Lokhande V, Lokhande A, Lokhande C, Kim JH, Ji T. Super capacitive composite metal oxide electrodes formed with carbon, metal oxides and conducting polymers. J Journal of Alloys Compounds. 2016; 682: 381-403.

[50] Liao Q, Li N, Jin S, Yang G, Wang C. All-solid-state symmetric supercapacitor based on Co3O4 nanoparticles on vertically aligned graphene. ACS nano. 2015; 9: 5310-5317.

[51] Wang X-f, Ruan D-b, You Z. Pseudo-capacitive behavior of cobalt hydroxide/carbon nanotubes composite prepared by cathodic deposition. Chinese journal of chemical physics. 2006; 19: 499.

[52] Ryu KS, Kim KM, Park N-G, Park YJ, Chang SH. Symmetric redox supercapacitor with conducting polyaniline electrodes. Journal of Power Sources. 2002; 103: 305-309.

[53] Gupta V, Miura N. High performance electrochemical supercapacitor from electrochemically synthesized nanostructured polyaniline. Materials Letters. 2006; 60: 1466-1469.

[54] Huang Y, Li H, Wang Z, Zhu M, Pei Z, Xue Q, Huang Y, Zhi C. Nanostructured polypyrrole as a flexible electrode material of supercapacitor. Nano Energy. 2016; 22: 422-438.

[55] Sharma R, Rastogi A, Desu S. Pulse polymerized polypyrrole electrodes for high energy density electrochemical supercapacitor. Electrochemistry Communications. 2008; 10: 268-272.

[56] Manjakkal L, Pullanchiyodan A, Yogeswaran N, Hosseini ES, Dahiya R. A wearable supercapacitor based on conductive PEDOT: PSS-coated cloth and a sweat electrolyte. Advanced Materials. 2020; 32: 1907254.